

COMMISSION OF THE EUROPEAN COMMUNITIES

industrial health and safety

Technical control of pollution in the iron and steel industry

Research progress report
30th June 1977

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Notice to the reader

This report covers the research work carried out in the period 1972-1977, and contains summaries of the various projects on air pollution control and the treatment of wastes.

INTRODUCTION

This report is the third 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 Coal and Steel 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 first research on methods of controlling air pollution in the iron and steel industry - subsidized by financial aid from the ECSC - began in 1957. At that time the main problem was to protect workers at their workplaces.

(*) - Report "Technical control of atmospheric pollution in the iron and steel industry", June 1968.

- Report 30 June 1972 (Eur.4921)

The massive increase in oxygen steel plants which began at this time resulted, however, in the urgent need to develop new techniques in order to reduce the quantities of brown fume emitted into the atmosphere by the converters. (*) The consequence was intense research in this sector leading to important developments which are now found throughout the world.

A second research programme (1967-1973) comprised a series of projects principally concerned with controlling the atmospheric pollution caused at the various stages of production and by the various steel treatment processes. However, this programme also included certain laboratory research projects on the physical and chemical characteristics of the dust, gas and fume emitted.

At present, the objectives of pollution control in the iron and steel industry are incorporated in the third programme entitled "Technical control of pollution in the iron and steel industry" (1974-1978) (**)

Thus the total financial aid granted up to now by the ECSC to research of this type amounts to some 17 million European units of account.

Unlike its predecessors, the third programme is not solely concerned with atmospheric pollution, but also pollution of waste water and some aspects of noise control. Furthermore, an important chapter is devoted to the treatment of waste matter, - utilization, processing, recycling or disposal. The evolution of the research objectives in the iron and steel industry can be traced over recent years by observing the relative importance assumed by the treatment of water and waste matter in the development of this programme.

Of the total aid granted until now under this programme, 14% has thus been for problems concerning liquid effluents (above all from coking plants) and 27% for the treatment of waste matter.

(*) - In 1958, the production of oxygen steel in the Europe of the Six was 600 000 metric tons (1% in total), in 1967: 25 million metric tons (28%). In 1975, for the Europe of the Nine, it rose to 73.2 million metric tons (58%).

(**) - Official Journal no C 92 of 6 August 1974

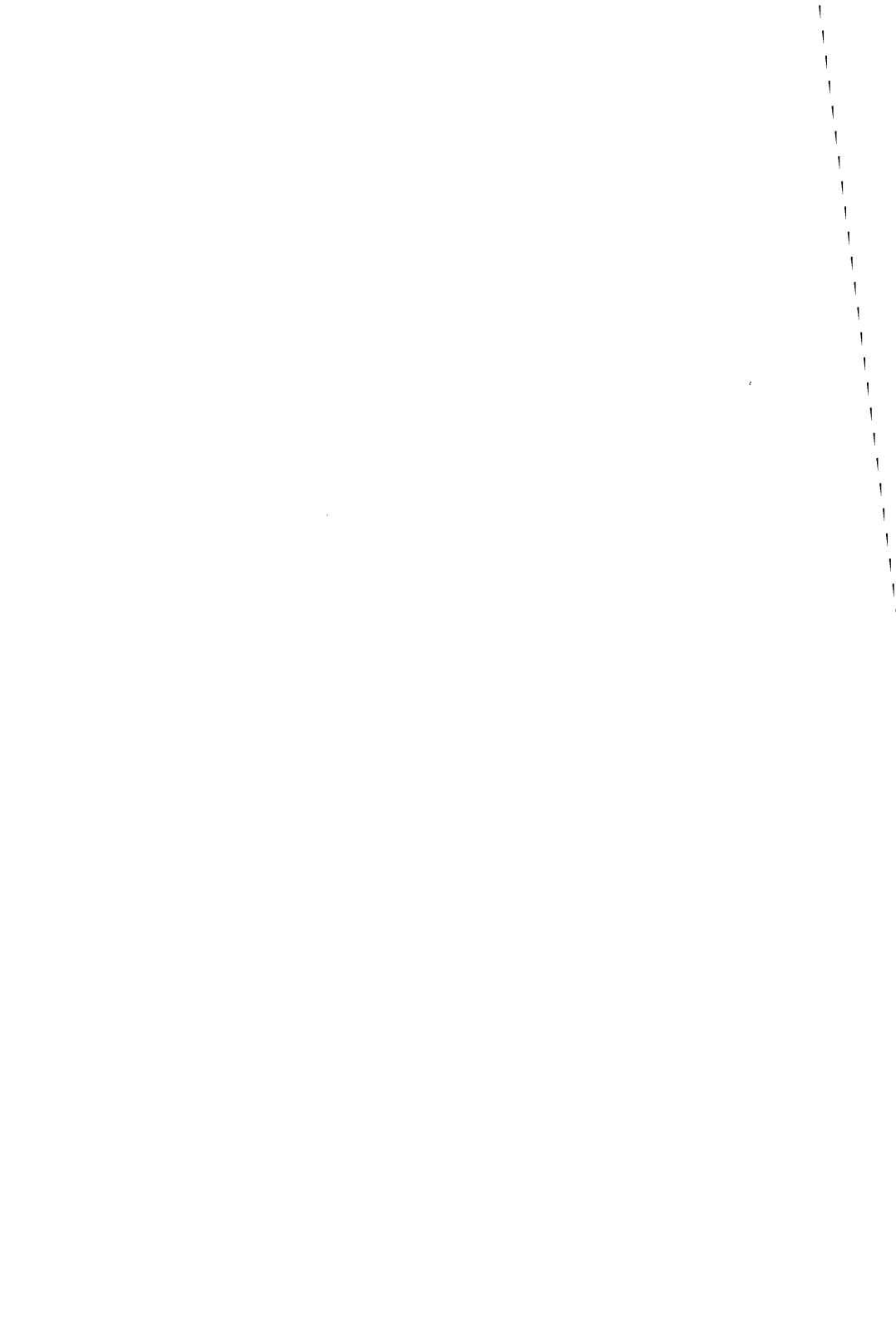
The desire of the industrial world to find practical methods to improve the environment was demonstrated by the large number of persons who participated in the conference "Quality of the environment and the iron and steel industry" held at Luxembourg on 24-26 September 1974. (*)

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 "Euroabstracts" publications. (**)

Reports follow on a total of 38 research projects, divided up into four thematic groups and arranged within these in alphabetical order. Most of them still come under the second programme, but they do also include - in particular in connection with the residue and waste problem - projects from the third programme.

(*) Eur. 5482 - Pergamon Press

(**) Office for Official Publications of the European Communities,
P.O.Box 1003, Luxembourg.



CHAPTER ITESTING, IMPROVEMENT AND DEVELOPMENT OF EQUIPMENT AND
PROCESSES FOR DETERMINING AND MEASURING AIR POLLUTION

Grain analysis of dusts with grain size less than $1\ \mu\text{m}$

(Institut für Mechanische Verfahrenstechnik der Universität Karlsruhe,
Study PS 157)

A more accurate knowledge of the grain size distribution of dusts with grain size less than $1\ \mu\text{m}$ would be extremely useful, for both technical and medical reasons. The methods suitable for measuring grain size distribution with this degree of fineness, and initial experiments with a sedimentation balance and an ultra-centrifuge, have already been described in EUR 4921.

In the next part of the project the theoretical basis for a process of sedimentation in the centrifugal field was developed.

In addition, practical tests were carried out in the laboratory to confirm the theoretical assumptions.

With apparatus combining a sedimentation centrifuge and a photometer it was possible to carry out comparative measurements of particle size in the size range from 0.4 to $5\ \mu\text{m}$ in 15 minutes, but absolute measurements of particle size are not yet possible.

A further study, using various different dusts from iron and steelworks, is now in progress.

Application of count efficiency curves to improve the accuracy, reproducibility and comparability of dust measurements at works
(Institut National de Recherche Chimique Appliquée, Paris, Study PS 167)

Microscopic counting methods are often used to assess dust conditions. It is known that the results of dust counts can vary considerably, as they are primarily a function of the specific operating conditions, that is of parameters which depend on the optical equipment used and the operating staff. Moreover, the grain sizes of dust collected at one working place often vary, especially in long-term studies and studies of dusts from different sources.

Because of the interplay of these factors, the results of microscopic counts cannot always be relied upon completely when assessing the development of dust conditions over a period of time, or comparing dust measurements at different works or in different countries.

There are, then, two sets of contributory factors which are in many cases unknowns - the microscopic and the granulometric factors.

Several of the research projects sponsored by the ECSC have helped to provide a more accurate knowledge of the first set of contributory factors. But granulometric studies are extremely expensive, as the outlay for the instruments and working hours required to measure dust grain sizes is so large that the advantages of the counting method are outweighed. Dust measurement by particle counting was introduced because it was a process that could be widely used and carried out by staff with only a medium level of technical expertise.

The aim of the research project was to establish formulae which could be used to compare particle counts with each other, once certain basic determinants for the microscopic and granulometric parameters are known.

For studies of dust from mines, a suitable formula permitting such comparisons was established. It is as follows :

$$E = - 20 \cdot (NA) + 33 \left[\% \right]$$

where

E is the deviation between the number of particles actually present and the number of particles measured with an optical instrument of slot width (numerical aperture) NA. This means that particle counts of dusts from mines can be compared with each other if the numerical aperture of the optical instruments used is known.

The findings of this study indicate that the numerical aperture should not be below 0.4, or the degree of uncertainty in the comparisons will be too great. Different particle counts can only be compared by this method if the standard grain size distribution is given for each of the dusts studied.

If dusts collected at working places in the iron and steel industry are studied without details of the grain size distribution, the various particle counts cannot be harmonized. But the model developed in this study enables researchers to gain some preliminary data on grain size by carrying out particle counts for one sample with two instruments and different numerical apertures. The result obtained can then in turn be compared with the findings of tests carried out in the same way elsewhere.

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 T.N.O. Delft, Study PS 175)

The results of particle counts can be influenced by various factors. A better understanding of these influences would make it possible to avoid mistakes in dust particle counts or to make allowance for them, to give more precise results than hitherto.

In this research project the influence of the following factors on particle counts was therefore studied :

1. Influence of the medium in which the dust particles are held during counting.
2. Influence of overlapping of individual dust particles. Overlapping has the effect of making several small dust particles look like a single, smaller particle when the sample is counted.

The research showed that overlapping of individual particles is attributable to three mutually independent factors. These are:

1. The surface density of the dust on the filter.

To keep the error due to overlapping down to 5%, the number of particles on the surface should not represent more than 2.5% of the total. In practice the number of particles on the surface is usually far higher, and it was therefore necessary to develop a special sampling device with extremely short exposure times (0.1-10s).

2. Conglomerate formations in the atmosphere.

This aspect will be investigated in connection with Study PS 209 using holographic techniques.

3. Subjective interpretation by the technician

When samples are counted under the microscope, subjective interpretation by the technician responsible for counting may significantly affect the result. This applies particularly to counts of dust aggregates. Counting methods must be found which make it possible to eliminate subjective interpretations as far as possible.

Samples were taken from a test chamber in which a monodispersed polystyrene latex aerosol was produced. As the samples were prepared, air was sucked through a filter with a slot-shaped aperture. With this arrangement it was possible to prepare successive samples with different percentages of particles on the surface, with exactly the same apparatus, simply by rotating the aperture.

As working parameters, percentages of 1, 2, 4, 8, 16 and 32% of particles on the filter surface were taken.

Three types of apparatus were used for analysis:

1. Optical microscope;
2. Scanning electron microscope;
3. Quantimet linked with an optical microscope.

In addition to these tests to prove the "overlapping theories", work was done on the design of an experimental system for taking dust samples from the fume ducts of a sinter plant. The results of these tests are an illustration of how theories can be applied to iron and steel industry practice.

The probe developed for taking dust samples in fume ducts was tested for efficiency of operation. Because of the conditions peculiar to fume ducts (high temperature, very high dust concentrations, aggressive acid gases, etc.) there were numerous difficulties. Ways of solving the

problems mentioned had in fact been found by the middle of 1975, but, owing to other difficulties encountered, it has not yet been possible to complete this study.

Determination of the size and distribution of suspended particulate in the air by holographic methods.

(Instituut voor Gezondheidstechniek T.N.O., Delft, Study PS 209)

The suspended particulate (dust) in the air is normally studied by using instruments which measure the amount of dust present in an aspired air sample. The amount of dust found is partly dependent on airflow patterns in the vicinity of the aspiration probe, and hence the dust level measured is dependent on the instrument used.

In practice this has meant that considerable differences are observed between results obtained with different dust measurement instruments, and it is thus extremely difficult to make comparisons between studies carried out with different measurement instruments.

Basically there are two ways of obtaining comparable measurement results :

1. By developing a measurement method which has no effect on the quantity observed, or whose effect is so slight that it may be neglected.
2. By correcting the errors arising from the type of sampling method (see PS 210).

In this project researchers studied a measurement method for determining the size and distribution of dust particles that has a negligible effect on the quantities observed. The method is based on holography, a technique for producing reproducible images of three-dimensional objects.

After initial studies of the theoretical aspects of holographic methods, holograms were produced of dusts of known composition in a dust chamber.

It was found that the concentrations of dust larger than $5\mu\text{m}$ measured by holographic methods differed considerably from those obtained by examination of membrane filter samples under the optical microscope. The holographic particle counts per cm^3 were larger in all cases.

In subsequent tests, attempts were made to modify the laser source used to produce the holograms so that dust particles with a diameter of less than $5\mu\text{m}$ could also be registered. This involved considerable difficulties and the research project had to be prolonged. The final conclusions were as follows :

- The use of holography to determine the grain size and distribution in air of suspended dust particles has a number of advantages:

- a) the spatial distribution of the particles can be determined,
- b) particles do not have to be collected by aspiration, which can distort the size distribution of the sample.

- However, the holographic method has a number of drawbacks:

- a) the reading-off process is very time-consuming,
- b) small particles ($1-5\mu\text{m}$) can only be studied within a test area very close to the photographic plate.

Because the space between the particles and the hologram has to be very small, it would be impossible in most practical situations to prepare holograms of particles $1-5\mu\text{m}$ in diameter.

- c) It is important that the laser beam does not have to travel too far through dust before reaching the area tested, as this can distort the intensity distribution and lead to very high background noise on the hologram plates, making images of small particles unrecognizable.

Comparative study of optical processes and sedimentation
processes for determining grain size in dust samples

(Institut National de Recherche Chimique Appliquée, Paris, Study PS 194)

The results of granulometric analysis depend to a large extent on the analysis method used. Hitherto it has been virtually impossible to compare grain size distributions with each other unless it is absolutely certain that the same analysis method has been used and unless, moreover, the possibility of human error (mistakes by operating technicians) has been excluded as far as possible.

The aim of this study was to provide a theoretical solution to the problems encountered without, initially, taking account of experimental difficulties.

The final report explains, first of all, why different grain size distributions are bound to exist as a function of the analysis method.

The conditions under which the number of different grain size distributions can be reduced, and under which different distributions can be made comparable, are outlined, together with a method for representing the grain size distribution in the form of a matrix, and a mathematical method for comparing grain size distributions.

Tests to determine the number of 0.5 - 5 μ m quartz particles
in a dust sample by means of interference microscopy

(Instituut voor Gezondheidstechniek T.N.O., Delft, Study PS 208)

There is as yet no satisfactory routine method for determining the number of quartz particles in respirable dusts.

This is all the more regrettable because the size of the quartz surface of dust particles in the respirable fraction is generally believed to be responsible for the silicogenic effect of the dust. The surface area of the dust particles is, however, more a matter of grain size distribution than of percentage weights.

This study was divided into two parts:

Part 1: Fundamental research to decide whether interference microscopy was a suitable method for counting quartz particles in a dust sample.

Part 2: If good results were obtained in Part 1, optimization of the process.

Two different methods may be used to decide whether identification of quartz by interference microscopy is feasible. They are:

1. Interference microscopy in incident light.

The main point to be studied here is the alterations in intensity which occur in the interference image of a quartz particle when it is in an alternating-current field.

2. Interference microscopy in transmitted light.

Quartz shows optical rotation and research is being done to find out whether this property can be used to distinguish quartz particles from other dust components.

Despite intensive efforts on the part of the research team engaged on this project since the end of 1972, and repeated extension of the project, which had originally been scheduled to take two years, the study had to be abandoned in the middle of 1976 without achieving its object. The effects anticipated on the basis of theoretical considerations were not observed. The research institute hopes to trace the causes, using its own funds, and will then inform the ECSC of the research results.

Study of the way in which the dimensions of dust particles can influence the result of airborne dust measurements with an aspiration probe
(Instituut voor Gezondheidstechniek T.N.O., Delft, Study PS 210)

To determine the size distribution of particles in an aerosol, samples are normally taken from an air-dust mixture. When samples are taken in an enclosed area, i.e. a wholly or partially enclosed space, isokinetic aspiration is often not possible because there are no air currents. Comparative measurements with different sampling instruments frequently differ considerably from each other.

In this research project, the research workers studied the movement of dust particles in the flow field of aspiration probes, to establish a better basis for the correction of errors due to the sampling method.

The research work involved:

1. calculating particle trajectories in the region of aspiration probes;
2. experiments in a dust chamber.

In the first stage of the work a simplified model was used to calculate the particle trajectories. It was assumed that the flow resistance of the particles would obey Stoke's Law, and that the sample was being drawn into a point-shaped probe. If the inertia of the particles is disregarded, the trajectory equation can be solved analytically.

However, if the inertia of the particles is taken into account, the trajectory equation can no longer be solved analytically; a numerical approximation method is given which can be used to solve these equations.

The experimental studies have so far been held up because of difficulties encountered in producing monodispersed test dusts with sufficient accuracy.

Special attention was given to the programming of the estimated trajectories of particles in the flow field of a slot-shaped probe.

The degree of aspiration with various Stokes's numbers was calculated for the upper and lower edges of the probe. The result indicated that the degree of aspiration is mainly influenced by losses at the upper edge. Here it was assumed that particles which touched the walls would adhere to them. The calculations also indicated that with slot-shaped probes, unlike point-shaped probes, the degree of aspiration does not depend solely on the Stokes's number.

The electronics of a laser speed monitoring system have now been developed to a stage where the monitoring system can be tested for plotting particle movements.

Direct and non-destructive analysis of pollutants from
the iron and steel industry

(Laboratoire d'Etude et de Contrôle de l'Environnement Sidérurgique,
Maizières-les-Metz, Study PS 232)

It is important to have as complete a knowledge as possible of the type and origin of atmospheric pollutants, both for medical and ecological reasons and because of the legislation currently in force.

In this research project, processes for physical analysis were studied in order to gauge their suitability for rapid and economic analysis of samples, which often consist of very small quantities of material.

The following processes were investigated:

- X-ray fluorescence spectrometry,
- optical spectrometry,
- neutron activation,
- flame photometry, and
- atomic absorption,

and the research findings indicated that analysis of thin filter coatings by X-ray fluorescence is the only viable method.

If filter coverage is not in excess of 0.3 mg/cm^2 , the radiation intensity of an element is proportional to the quantity of the element on the filter.

Comparative measurements with different analysis techniques have confirmed the viability of the method proposed.

Adjustment and calibration of systems, particularly optical ones, for the continuous monitoring of dust emissions from iron and steel plants (Laboratoire d'Etude et de Contrôle de l'Environnement Sidérurgique, Maizières-les-Metz, Study PS 230)

At present there is a lack of inexpensive systems for continuous measurement of the dust content of waste gases.

In this study various optical measurement systems providing continuous measurements of dust levels were tested. The results were compared with those obtained using beta-radiation devices and an IKOR device.

The tests were carried out in the waste gas system of a sinter plant, and further tests are planned in steel works and a coking plant.

The tests conducted so far indicate that optical dust measurement systems are suitable for measuring the dust content of clean gas after dry dedusting but that, given the present state of the art, they are not suitable for measuring dust levels after wet cleaning.

The calibration of optical measurement instruments presents serious problems because the quantity and composition of dust formed fluctuates considerably in all metallurgical processes, depending on the operating conditions.

It is not possible to obtain a single calibration curve for optical measurement systems - instead one obtains clusters of curves, with the various dust properties as parameters.

Consequently, optical measurement systems are in most cases only suitable for qualitative monitoring, e.g. to indicate whether levels are below the permitted maximum in a certain plant.

Optical measurements systems are only suitable for quantitative measurements of dust levels when the conditions under which they are used are known and can be checked.

Continuously recording measurement of the solids in gas-dust mixtures with the 'Konitest'

(Betriebsforschungsinstitut des Vereins Deutscher Eisenhüttenleute, Düsseldorf, Study PS 159)

The basic measurement principle of the Konitest, and initial research findings, have already been described in booklet EUR 4921. The final report, now available, gives the following information:

The tests in a dust experimenting chamber and at various dust discharge points have shown that the reading on the Konitest instrument is not only dependent on the dust content but is also influenced by the following factors:

- the design of, and contact material used for, the energizer tube
- the volume of gas flowing through the energizer tube
- the chemical composition of the dust
- the grain size distribution of the dust
- the electrical charge of individual dust particles
- the moisture content of the gas.

The tests carried out in the research project yielded the following results:

The most suitable material for the energizer tube in a Konitest device for measuring the dust content of 'brown fume' is steatite.

In laboratory tests there was a linear relationship between the Konitest reading and the dust content, but it is not always reproducible. This is most probably due to dust deposition on the energizer tube and variations in the properties (such as grain size), the chemical composition and the electrical charge of the dust particles.

Measurements of the dust concentration in LD converter fumes on the clean gas side of an electrostatic precipitator were used as a basis for characteristic calibration curves. However, when the electrostatic precipitator was switched off these characteristic curves were no longer applicable.

When the instrument was used to monitor dust levels in the gas discharge flue of an open hearth furnace and the gas exhaust system of a wet flame scarfing plant, no clear relation was found between the actual dust content and the Konitest reading.

Theoretical studies have shown that the grain size of the dust has a considerable influence on the Konitest reading. The reason for this is that, the smaller the dust particle, the larger the electrical charge per unit of particle mass.

On the basis of these findings, the following conclusion was drawn:

In its present state of development, the Konitest instrument used in this research can only provide reliable quantitative measurements of dust levels in waste gas systems in certain special cases. Precise, reproducible calibration is difficult because of the large number of limiting factors (as described above). The Konitest instrument can however

be satisfactorily used for measurements where a high degree of accuracy is not required, especially for comparative measurements.

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-les-Metz, Study PS 231)

The number of monitoring networks in the vicinity of iron and steel works is increasing steadily. Often the analysis of measurement data from monitoring networks is unsatisfactory, for a number of reasons, but analysis could be greatly improved if use were made of statistical methods of the type already developed for use in the fields of sociology and economic sciences. The aims of this research project are therefore:

- to improve mathematical methods and utilize compatible data sources for the analysis of measurement data;
- to test methods which have already been put into practice in many individual cases in French and other monitoring networks;
- to develop analysis programmes that are as comprehensive as possible;
- to outline priorities, based on practical instances, for the control of environmental pollution caused by the iron and steel industry.

So far, the project has dealt with data from a measurement network with the following structure:

- 50 measurement points for measuring dustfall (monthly sampling, with analysis and gravimetric measurement of approximately 15 component substances);
- 9 measurement points for measuring suspended particulate (dust) (weekly sampling and analysis of six component substances);
- 30 'Diam' plates for measuring dustfall
- 26 measurement points for measuring gaseous constituents, especially fluorine, with daily measurements of concentrations;

- 30 fixed measurement points for measuring gaseous fluorinated constituents
(monthly concentration measurements);
- meteorological data (wind direction and wind speed) expressed as three-hourly values.

Measurement of fluorine in emissions from iron and steelworks with the Orion Research Inc. specific fluorine ion analysis electrode (Clinica del Lavoro dell'Università di Milano, Study PS 216)

Measuring fluorine by the conventional colorimetric method involves certain difficulties because of the presence of iron, aluminium, phosphates and sulphates, which are always found in the atmospheric pollutants given off by iron and steelworks. To eliminate these difficulties, the colorimetric method makes use of the volatility of hydrofluoric acid in an acid medium, separating the constituents by microdiffusion.

When fluorine is measured by means of an electrode sensitive to fluorine ions, it is not necessary to separate the fluorine from the accompanying substances. This measurement technique depends on the ability of the fluorine ions to pass through lanthanum crystals. If two electrodes are introduced into a solution containing fluorine, one being a reference electrode and one being covered with lanthanum fluoride crystals, the potential difference between the two electrodes is proportional to the concentration of fluorine ions in the solution.

The electrode method would appear to have considerable advantages over microdiffusion and colorimetric analysis, being simpler and easier to use.

The instructions for use given by the manufacturer of the analysis electrodes were modified slightly for use in studies of the atmosphere around iron and steelworks. The results were compared with the results obtained using colorimetric methods. With fluorine concentrations of between 0.05 and 0.3 μg per ml of solution, the mean deviations were

+ 3%. With fluorine concentrations below 0.05 $\mu\text{g}/\text{ml}$ the analysis electrodes gave markedly more reproducible results than the colorimetric method.

The procedure developed on the basis of this research has been incorporated in the implementing order issued to industry by the Italian Ministry of Health under the law on measures to prevent air pollution.

CHAPTER IIMEASUREMENT OF AIR POLLUTION AT WORKPLACES
AND IN THE IMMEDIATE VICINITY OF STEELWORKSSystematic determination of different air pollutants from a coking plant
in an iron and steel works complex(Centre Belge d'Etude et de Documentation des Eaux, Liège, Study PS 140)

The main interim results of this research project have already been described in the Progress Report (EUR 4921). Some further details are given below, taken from the final report on the project which has since been completed.

1. Air pollution by dust at different working places in a coking plant

It has once again been confirmed that when assessing air pollution at working places a distinction must be made between the quantity and quality (type) of particles emitted.

In the working areas where coal is loaded, unloaded and prepared, the total dust concentrations measured amount to at most 1/10 of the MAC *) of 15 mg/m^3 stipulated by American industrial hygienists. The quartz content of the fine dust is so low that there is no risk of silicosis for the persons working in this area.

In the areas in the immediate vicinity of the coke ovens, the concentrations of dust containing tar are frequently in excess of the maximum admissible concentration. There is no risk of silicosis, as the quartz content of the dust is low, but coal tar contains many polycyclic hydrocarbons, including 3,4- benzpyrene, which is carcinogenic.

*) Maximum admissible concentration at the working place.

The dust concentrations measured in the coke loading and screening areas are above the MAC value, but there are no permanent working places in these areas.

2. Air pollution by gases at working places directly linked with the coking process

With only one exception the levels of gaseous air pollutants found at working places in the coking plant were not high. The exception was the cab of the charging larry car, where CO concentrations of 10-260 ppm were measured, although only for short periods.

3. Type and concentration of certain hydrocarbons emitted in the coking process

Special analysis methods had to be developed to measure the hydrocarbons present. Of the hydrocarbons studied - methane, benzene, toluene, xylene, naphthalene, 3,4-benzopyrene and acridine, only naphthalene was found to be present in quantities approaching or sometimes exceeding the maximum value stipulated by the ACGIH^{*)}.

4. Level of air pollution in the immediate vicinity of the coking plant

Air pollution was monitored in the vicinity of the coking plant and, by measuring the concentration of tar-containing dust, an indication was obtained of the proportion of pollutants traceable to the coking plant.

These studies showed that emissions from the coking plant account for approximately 25% of total air pollution some 500 m away from the plant, although the exact proportion depends on the prevailing weather conditions.

*) American Conference of Governmental Industrial Hygienists

Controlling dust extraction from charging emissions where preheated coal mixes are used
(Centre d'Etudes et Recherches des Charbonnages de France, Paris, Study PS 240)

Coke-oven charging with dried, preheated coal has two technical advantages:

- widening of the range of coal which can be used for manufacturing metallurgical coke;
- reduction of coking time, i.e. increased production capacity.

The combination of coal preheating with a pneumatic steam-entrained charging system also has potential advantages with regard to the control of emissions during charging operations. In order to be able to give definite information on air pollution as a function of the charging system, three methods - ramming, feeding, preheated charge - were subjected to a comparative investigation.

In order to collect the waste gases containing dust, extractor hoods were placed at the coke oven outlets, and the gases given off were extracted and led through a chimney. This made it possible to remove a sub-flow and analyse it for its tar and dust content.

The tar and dust levels were compared with the total charge, with the following results:

- charging with preheated coal by pneumatic entrainment with superheated steam (COALTEK process):
0.4 g of tar and 0.4 g of dust per t of charge coal
- feeding with wet charge:
emissions were measured in a modern coking plant equipped with charging cars fitted with washing equipment.

The measurements show considerable accumulations.

12 - 55 g of tar per t of dry charge coal

23 - 70 g of dust per t of dry charge coal

- ramming:

during measurement of the emissions, it was not possible to determine the emitted gases fully. The following figures were calculated as approximate values:

13 - 39 g of tar and 17 - 33 g of dust per t of dry charge coal.

Since in the case of pneumatic charging with preheated coal there is no direct contact between oven chamber and the outside air at any time during the charging operation, an emission can only occur through leakages (e.g. at the oven doors).

The results of the measurements show that, with regard to charging emissions, pneumatic charging of coke ovens with preheated coal has clear advantages.

Continuously recording measurement of dust levels in iron and steel works with the 'Konitest' and measurement of the toxicity of certain dust samples

(Bayerisches Landesinstitut für Arbeitsschutz, München, Study PS 158)

As explained in greater detail elsewhere (EUR 4921, PS 159), the Konitest instrument makes use of contact electrical interactions between solid particles and an energizer tube through which the gas-dust mixture investigated is drawn, to provide virtually instant continuous measurement of the dust concentration.

In this project further development work on the instrument aimed at providing direct measurements of the concentration of respirable fine dusts, as defined by the Johannesburg Convention, ran parallel with measurements of the dust concentrations at various working places in iron and steel works. So that only the fine dusts capable of entering the alveoli are studied, the coarser dust must first of all be separated out from the air drawn into the instrument. With the Konitest, a pre-cyclone is used for this purpose.

The measurements were intended partly to test the effects of certain modifications to the Konitest instrument, and partly to measure the actual dust burden at the following working places:

a) Basic slag grinding plant

Here dust concentrations in the ambient air of 18.1 mg/m^3 were measured; the fine-dust component (grain size of less than $5 \text{ } \mu\text{m}$) was 1.23 mg/m^3 . The quartz content was below the detection limit and the concentration of manganese and vanadium was 0.28 mg/m^3 . In other words, all the values were below the MAC values.

b) Grey iron foundry

At the working places covered, total dust concentrations of $15.3 - 32.8 \text{ mg/m}^3$ were measured. The fine dust concentration was between 0.87 and 1.36 mg/m^3 . The fine quartz dust concentration fluctuated between 0.11 and 0.23 mg/m^3 , i.e. in the region of the MAC value of 0.15 mg/m^3 .

c) Scrap yard

Dust concentrations of 4.2 to 6 mg/m^3 were found at working places in this area. The dust consisted mainly of particles larger than $10 \text{ } \mu\text{m}$. The quartz content was below the detection limit.

The dust measurements in iron and steelworks, and the development work aimed at direct measurement of dust capable of entering the alveoli, were interrupted by the sudden death of the research project leader in 1975. Work on this research project was resumed in the middle of 1976.

Determining the concentration of silicogenic, toxic and obnoxious dust at working places in the iron and steel industry

(Staubforschungsinstitut des Hauptverbandes der gewerblichen Berufsgenossenschaften, Bonn, Study PS 169)

In this research project the Staubforschungsinstitut studied selected working places in three different iron and steel works.

The working places studied were in the sinter plant, the preparation bays for pig iron and crude steel ladles, and the foundry or fettling plant. The dust levels were monitored for a 4-hour period, at least four times at different times of year.

The findings of the dust sample analyses were compared with the MAC values for fine quartz dust (0.15 mg/m^3) and quartz-bearing fine dust (4 mg/m^3), and with the guide value (recommended maximum) for total dust affecting the lungs and airways (15 mg/m^3).

The research institute has also introduced an evaluation index. This index is the quotient of the fine dust (or fine quartz dust) concentration measured and the relevant guide value or MAC. If this dimensionless number > 3 , it is statistically certain, even with only one measurement, that the MAC is being exceeded. If the dimensionless number $< 1/3$, the level is certainly below the MAC value, even if only one measurement has been made. In between these two figures, the result and its relationship to the MAC value must be checked by repeating the measurement.

The four series of measurements from each of the three iron and steel works indicate that:

1. Sinter plant

In all three sinter plants studied, the level of fine quartz dust in the ambient air at the working places was below the MAC value.

At some points the total dust concentration was above the guide value of 15 mg/m^3 but these measuring points were not permanent working places and workers only visit them briefly for routine checks.

2. Ladle relining

Relining pig iron or molten steel ladles will, depending on the method used, involve considerable exposure to total dust and exposure to quartz-bearing dust in excess of the MAC value. Dust exposure is particularly high during the breaking-out of the old lining.

3. Fettling plant

The dust levels at working places in fettling plants depend primarily on the process used.

In one of the works studied, a hydro blast fettling system was in use and the levels of quartz-bearing and total dust were well below the MAC levels.

In the other two plants, however, the quartz component and the total dust concentration were (depending on the particular operations) above the MAC levels.

Investigation of air pollution at different places of work in Luxembourg iron and steel works and in their immediate environment (Mineralogical Laboratory of the Natural Sciences Museum, Luxembourg, Study PS 181)

The first part of this project, which involved measurements of dust precipitations in the vicinity of an iron and steel works, has already been described in considerable detail in EUR 4921. The following information may be added, on the basis of the final report which has since been submitted :

Dust measurements in two iron and steel works showed that the situation was as follows in the working places with the highest dust concentrations :

- Ore preparation

As the plant used for this purpose is automated and only attended for short periods by a small number of workers, there is virtually no danger to health.

- Blast furnaces

The workers responsible for tapping the blast furnace are exposed to dust hazards.

- Steel making plant

Operatives working in the vicinity of manganese furnaces and Bessemer converters are exposed to dust hazards.

SO₂ pollution in the immediate vicinity of the iron and steel works was measured with Wösthoff devices. The levels fluctuated between 0.5 and 3.8 ppm within a 24-hour period. The measurement period of eight months is thought to be too short to yield any definitive indications of the connection between the measurements obtained and weather conditions.

The SO₂ measurements carried out at the working places showed drastic and abrupt fluctuations in SO₂ levels which cannot be accounted for by changes in working procedures or conditions. It seems likely that these irregularities are due to the measurement method.

Investigation of the distribution of air pollutants in workshops by air currents arising from heat, draughts and fans
(Instituut voor Gezondheidstechniek T.N.O., Delft, Study PS 176)

Pollutants (especially those in the form of small particles or droplets) which enter shops during industrial processes are propagated primarily by and with air movements.

Before one can successfully control the propagation of pollutants in a shop, one must have information on the pattern of air movements found there.

The processes used in the iron and steel industry usually give off a relatively large amount of heat, as well as certain quantities of pollutants, into the atmosphere. This leads to temperature changes which create air currents in the shop.

Where heat and/or pollutants are given off in a shop, attempts are made to limit the unpleasant and harmful consequences by means of ventilation. The type of ventilation used may be natural or mechanical. For the purposes of this study, air measurements were carried out in a strip tinning shop, in order to :

- determine the pattern of air currents in the shop and find out which factors caused the pattern,

- measure the temperature distribution in the shop and show how it is related to the pattern of air currents,
- register the distribution of dust concentrations.

The following conclusions may be drawn from the measurement results :

- there is a clearly marked and logical pattern of air currents in the shop. It is almost entirely attributable to the heat given off by the machines. External factors (draughts to and from windows and openings leading to adjacent shops) have only localized effects on the flow pattern;
- there is a clear relationship between the pattern of air currents, on the one hand, and the temperature and dust concentration distributions on the other. Again, the relationship is logical;
- it was found that the rate of air exchange in the shop could be fairly accurately determined by means of measurements. Evacuation of oil droplets was measured on this basis and found to be roughly equivalent to the estimated oil consumption of the lubrication system for the machinery;
- the results would appear to provide a suitable basis for model studies in these shops.

Experimental investigation into the dispersion pattern of a number of air pollutants (sedimentary dust, suspended dust and sulphurous waste gases) emanating from the iron and steel industry
(Istituto di Igiene-Università di Genova, PS 179)

The aim of the research is the experimental investigation of the dispersion of sulphur dioxide and sedimentary and suspended dusts in a large residential area in the vicinity of an integrated iron and steel works. The area studied lies in the Genoa region between the sea and the Ligurian Appenines, has an area of approximately 6 km² and a population of approximately 27 000. The main sources of emission are : household heating systems, motorized traffic and the largest industrial plant in the area, an integrated iron and steel works.

The investigations extended over a period of two years. Eight measuring points were set up in the area under investigation.

For the area as a whole an average sulphur dioxide level of 0.055 ppm*) was ascertained, with a minimum of 0.044 ppm and a maximum of 0.084 ppm. Analysis of the SO₂ level as a function of the meteorological and seasonal conditions shows that it is affected to a great extent by household heating systems.

The suspended dust was determined by means of a densimetric procedure (optical control of a filter coated with dust). By means of parallel measurements the correlation between "densimetric" and "gravimetric" dust level was determined. The gravimetric suspended dust levels in the area investigated ranged between 0.135 mg/m³ and 0.193 mg/m³. The measured levels of sedimentary dust, the total of which increases in the summer months, fluctuate quite considerably between a minimum of 316 g/100 m² per month and a maximum of 2 214/100 m² per month.

Overall, the investigation shows the pattern of air pollution as a function of wind direction and wind speed in the area investigated.

No correlation could be shown in the test area for SO₂ exposure and dust exposure.

Dust emission during loading and storage of bulk goods

(Betriebsforschungsinstitut des Vereins Deutscher Eisenhüttenleute, Düsseldorf, Study PS 204)

When bulk goods are loaded, unloaded and stored in the open air a certain proportion of the material is carried away by the wind and can thus pollute the surrounding area. At present there are still considerable gaps in our knowledge regarding the quantity of dust blown away and the manner in which it is propagated.

*) parts per million = cc of gas/m³ of air

The aim of this study was to fill in some of these gaps. The study was in two parts :

1. Simulated tests
2. Tests under operational conditions.

In the simulated tests the researchers studied the mechanisms by which powdery and granular material is blown off conical dumps with widely varying dumping angles, grain sizes, crude densities of material and wind velocity. The tests were carried out first of all on still material, and then the loading and unloading processes were simulated.

The results of the simulated tests were supplemented by practical tests in bedding plants. For these practical tests, gravimetric dust concentration monitors were set up and the wind direction and wind velocity in the area studied were measured to provide information on the meteorological conditions.

On the basis of the test findings, a dimensionless reference figure for bulk goods was calculated, and can be used to estimate the specific blowoff losses from a dump.

This reference value for dust losses from fine-granular material in storage is determined by :

- the wind speed
- the bulk weight of the goods stored
- the average grain diameter of the material
- the dumping angle in the storage yard
- the grain form of the material stored.

Depending on the type of ore, type of dump and wind speed, losses can, under normal circumstances, be as high as $0.2 \text{ g/m}^2 \cdot \text{h}$.

Any losses during loading and unloading depend primarily on the moisture content of the ore. In other tests it was shown that with more than 1.1% moisture content there were no further ore losses, indicating that with natural moisture contents of above 5%, in normal circumstances, there would be no further ore blowoff during loading and unloading.

Open air measurements in the vicinity of an ore yard showed specific losses of 0.35 g/t of ore unloaded and stored.

Study of the effect of sinter plant charging and operating conditions on the dust content of sinter waste gas and the physical properties of the dust
(Rheinstahl AG, Bau- und Wärmetechnik, Gelsenkirchen, Study PS 218)

This research project was devoted mainly to establishing favourable charging and operating conditions which would help to reduce the dust emission of a sinter plant. The levels of SO₂, SO₃, Pb and Zn in the gas discharged from the plant under various charging and operating conditions were also measured.

The materials charged in sinter plants are fine ore, concentrates, blast furnace flue dust and mill scale.

The dust content was determined by gravimetric methods, obtaining samples by drawing off a fraction of the gas emitted.

Between June 1971 and December 1974, the effects of the charging and operating conditions in a sinter strand with a grate area of 60 m², on the levels of dust generated, the chemical composition and hence specific electrical resistance of the dust, were measured in 51 measurement series. 30 000 t of sinter were produced in the course of the tests. By incorporating other findings from sinter plants with grate areas of 150 and 400 m², it was possible to establish certain generally-valid interrelationships.

It was found that the factors which have the most decisive effect on the specific dust level are the travelling speed of the sinter strand and the fines content of the raw mix.

It was shown that the specific electrical resistance of the dust was, with a degree of certainty approximately 94%, a function of the chemical composition of the dust. The tests indicated that a twin cyclone dust collector filtered out 80-90% of the dust, compared with a dry electrostatic precipitator performance of 90-98%. But whereas the dust collected in the cyclone is virtually free of lead, zinc and alkalis, and can therefore be recycled without difficulty, the electric precipitator also filters out lead, zinc and alkalis, and these substances therefore accumulate in the cycle after a certain period.

In the future sinter plants will have to be equipped with desulphurization units as well as dedusting units and it is therefore probable that the "cyclone + alkali scrubber" formula will be both technically and economically more feasible than "electric precipitator + desulphurization unit" configurations.

Evaluation of the kind and quantity of emissions on operation of open-hearth furnaces in relation to the melting process
(Betriebsforschungsinstitut des Vereins Deutscher Eisenhüttenleute, Düsseldorf, Study PS 215)

Despite all the prognoses of a decline in open-hearth steel production, a substantial proportion of crude steel output in the future will in fact still come from open-hearth furnaces. The open-hearth melting shops remaining in operation have to be dedusted, and it was for this reason that work was done in this study on the incidence of different parts of the process on dust emission, dust composition and the precipitation capacity of dust from open-hearth furnaces working with a high scrap ratio, to obtain information that be put to use in the design of dedusting systems for open-hearth furnaces of this type.

In the open-hearth furnace the heat input to the charge, and hence the melting capacity, are dependent on the transfer of heat from the combustion gas to the surface of the scrap and conduction of heat through the scrap. The application of heat to the charge leads to the process-linked melting loss, and this is accompanied by further material-linked melting losses (which depend on the composition of the charge) caused by oxidation of non-ferrous materials in the charge. There is a linear relationship between the melting capacity in $\text{kg}/\text{m}^2 \cdot \text{h}$ and dust emission in kg/t crude steel when averaged over the whole period of the melt, with the composition of the charge as a parameter.

At the combustion temperatures generated in an open-hearth furnace ($> 1900^\circ\text{C}$) the sulphur in the oil burns off completely, to form sulphur dioxide. Although it is not usually possible for SO_3 to be formed directly, owing to the high combustion temperatures in the upper part of the furnace, it can nevertheless be formed from SO_2 by catalytic interactions with metallic dust deposits in the regenerators (e.g. Fe_2O_3). It is also probable that SO_2 is converted into SO_3 by reaction with the NO_x in the spent gases. It is therefore very likely that SO_3 will be found together with SO_2 in the waste gas from an open-hearth furnace.

When heavy fuel oil is burned nitrogen oxides are formed only from the nitrogen and oxygen in the combustion atmosphere, as the oil contains no atomic nitrogen. The composition of the charge is reflected in the composition of the dust emitted. In some cases zinc and lead compounds make up a larger proportion of the dust than iron compounds. The specific electrical resistance of the dusts studied is below $10^{10} \Omega \cdot \text{cm}$ at a waste-gas dew point of approximately 50°C , owing to the normal moisture during combustion of heavy fuel oil, and furnace temperatures of $> 250^\circ\text{C}$.

This gives some indications of the readiness with which dust can be precipitated in a dry electric precipitator and these will have to be confirmed in practical tests. Where cloth filters are used, various problems have to be reckoned with in view of the acidity of the dust and the dew point of sulphuric acid ($> 150^\circ\text{C}$). High-efficiency scrubbers are normally out of the question, partly because of the need for waste-water cleaning and slurry removal facilities and partly for reasons of cost.

Causes of dust formation during surface treatment of steels by flame scarfing and grinding
(Betriebsforschungsinstitut des Vereins Deutscher Eisenhüttenleute, Düsseldorf, Study PS 223)

More and more plants are being installed for the surface treatment of rolled products by flame scarfing or grinding, which gives off particulate emissions. The level of dust emission and the properties of the dust are to a large extent dependent on the composition of the steel processed.

The aim of this study was :

- to establish statistically reliable connections between dust levels, dust composition and grain size distribution, on the one hand, and the composition of the steel processed on the other, and
- to establish a correlation between the degree of efficiency of the dust extraction plant and the precipitation and impingement behaviour of the dust in the untreated gas.

The measurements on grinding machines were abandoned after a few preliminary tests, owing to the difficulties involved in carrying out experiments. Because of the overlapping of so many different variables, no clear correlations could be found. The extra work required to obtain universally valid results would have been beyond the financial means available and could not have been completed within the time specified for the project. The research work was therefore confined to flame scarfing machines.

The theoretical and experimental work showed that, apart from alloy components, all the other contributory factors considered affected dust levels proportionally to the scarfing losses.

These contributory factors are :

- flame scarfing speed
- temperature of materials treated
- oxygen pressure
- geometry of flame nozzles

- dimensions of materials treated
- surface condition of the material treated.

These factors only affect the dust levels indirectly, depending on the amount of scaling losses. The ratio of scaling losses to dust formation remains constant.

The alloy components of the steel, on the other hand, have varying effects on scaling losses and dust levels, and hence on the relationship between the two.

Of the principal alloy components used, the one which most affects dust levels is carbon. In the carbon range studied - from 0.02 to 1.05% by weight - the increase in the dust concentration was more than proportional.

In all, 420 dust measurements were effected in an ingot and a slab scarfing plant, and were then analysed by applying a regression estimate. From the regression analysis, it was possible to calculate the dust concentration likely to occur in the exhaust gas from a flame scarfing unit.

The capital costs and running costs for a total of 26 dust extraction systems were correlated with certain parameters, to provide an indication of the efficiency and suitability of the various alternative systems available.

The following alternatives were considered :

- pipe-type wet electrostatic precipitators with internal parts made of mild steel
- pipe-type wet electrostatic precipitators with internal parts made of stainless steel
- plate-type wet electrostatic filters with internal parts made of mild steel
- plate-type wet electrostatic precipitators with internal parts made of stainless steel
- venturi scrubbers.

In the light of the considerations outlined above, it was concluded that the plate-type wet electrostatic precipitator with internal parts made of stainless steel represented the most economic solution.

Rapid oxidation of SO₂ to sulphuric acid in the presence of iron oxide in moist air
(Institut National de Recherche Chimique Appliquée, Paris, Study PS 163)

On the basis of the final report now available, the following may be added to the information already given in EUR 4921 :

The oxidation of sulphur compounds in the atmosphere, and in particular the oxidation of SO₂, has serious consequences :

1. Oxidation converts SO₂, a substance of relatively low toxicity, into considerably more toxic compounds such as SO₃ or H₂SO₄.
2. The oxidation products of SO₂ are responsible for the formation of acid smog, which can cause considerable environmental damage.

There are three basic processes of SO₂ oxidation in the atmosphere :

1. Photochemical oxidation in the atmosphere (often in the presence of other air pollutants such as nitrogen oxides, hydrocarbons or other compounds).
2. Oxidation in smog particles (often in the presence of dissolved catalysts).
3. Oxidation on the surface of solid particles.

This research project dealt with the latter process, the solid particles in this case being iron oxide particles.

In order to reproduce actual conditions, the research project studied the oxidation of SO₂ solutions in the presence of suspensions of iron oxide. The following conclusions were drawn from the research findings :

- In the presence of iron oxide, solutions of SO_2 are oxidized into sulphuric acid. The oxides do not have a catalytic effect, but the sulphuric acid attacks the oxide and as a result the dissolved active Fe ions act as homogeneous-phase catalysts.
- This process occurs with Fe_2O_3 , Fe_3O_4 and Fe. The stronger the SO_2 concentration, the faster the process takes place. With SO_2 solutions of 10^{-3} Mol per litre almost all the SO_2 is oxidized in a few hours. (This strength of solution corresponds to that found in a very polluted atmosphere close to the source of emission or in some stack plumes).

The findings show that in unfavourable weather conditions (e.g. high humidity or fog) the processes described can lead to rapid oxidation of SO_2 if iron oxide dusts are present close to sources emitting SO_2 .

In further studies of the transformation of sulphur dioxide into sulphuric acid in relation to climatological data there was again found to be a strong correlation between the rate of oxidation and the dust concentration, and iron oxide was also present in this dust.

Study of the real composition of fluorinated substances emitted into the air from iron and steelworks, 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, Study PS 238)

Emissions of fluorinated substances have already been studied in a large number of research projects. But the investigation methods adopted hitherto have referred both to gaseous and solid fluorinated compounds, and the solid compounds can be in various forms ranging from aerosols to coarse dust.

The purpose of this research project was therefore to :

- study the composition of the various fluorinated compounds emitted from iron and steelworks (sinter plants, oxygen steelworks, electric-arc steelworks, etc.);
- determine the effective toxicity of the fluorinated compounds identified and monitored at different sources.

For analysis of the gaseous fluorine, an existing electro-chemical method was modified and improved to give more accurate results. Numerous calculations are necessary for this method and a computer programme was devised for this purpose.

For analysis of solid fluorine, the method involving acid treatment and production of HF had to be excluded because high concentrations of HF would have distorted the measurements.

X-ray diffraction was used to determine the fluorine concentration. The practicability of this method was proved by means of comparative analyses using dust from a bag filter at a sinter plant and samples from the sinter mix.

CHAPTER IIIINVESTIGATION AND DEVELOPMENT OF PROCESSES FOR TRAPPING AND
PRECIPITATING AIR POLLUTION, OR FOR REDUCING THE OCCURENCE
THEREOFPurification of toxic fumes produced during slag granulation
(Centre Belge d'Etude et de Documentation des Eaux, Liège,
Study PS 237)

The granulation of slag generates large amounts of water vapour, gases and fumes which contain sulphur and other compounds.

The aim of this project is to devise a technique for eliminating toxic substances that is compatible with the slag granulation process.

The following studies are in progress:

- Study of the nature and composition of gaseous emissions during slag granulation.
- Theoretical study and laboratory tests on ways of treating these emissions.
- Research on a system for collecting gas and fumes produced during slag granulation.

Research work to date has culminated in the development of an apparatus for instant and continuous measurement of SO_2 and H_2S . A device with a flame spectroscopic detector (FSD) was found to be the most suitable for this purpose.

To calibrate the instrument, it is necessary to produce stable gas mixtures in calibration flasks. It has been found to be necessary, for the low gas concentrations required, to check the composition of the gas before each calibration procedure.

Further experiments dealt with ways of extracting the H_2S without affecting the SO_2 content.

Experiments are now being conducted with mixtures of H_2S and nitrogen, as these have been found to be more stable than mixtures of H_2S and air.

Dust removal from CO-containing waste gases from oxygen blowing converters by means of electric filters

(Stahlwerke Peine-Salzgitter AG, Salzgitter, Study PS 199)

A report on this research project has already been published in booklet EUR 4921.

The research work has now been completed and the following points may be made:

By incorporating a new type of hoodless cooler stack which is inclined in relation to the converter axis, excellent results can be obtained with the dust extraction system based on the principle of 'suppressed combustion'. The need for careful adjustment of the air factor is the only slight limitation of the system compared with air cleaning systems with a separate gas collection hood or skirt.

Exhaustive measurements of the waste gas composition, using samples taken from the end of the boiler section, showed that the combustion reactions in the gas (especially the reaction $2 CO + O_2 \rightarrow 2 CO_2$) were all complete by the time the gas reached the end of the boiler. There is therefore no need for a further burnoff section after the waste heat boiler and before the first set of conditioning water sprays.

In the cooler stack the waste gas is cooled to a discharge temperature of approximately $1000^\circ C$. This means that the temperatures inside the waste heat boiler are always higher than the ignition temperature of the mixtures of gases present. The oxygen from the entrained air is almost completely converted to CO_2 in the presence of CO, before the waste gas enters the conditioning section.

There was no evidence of separate gas streams in the conventional sense, but the flow measurements indicated that at certain points the gas flow deviated considerably from a 'piston' flow pattern, i.e. that because of the highly asymmetric flow profiles, gases passing consecutively through the system will in fact be mixed with each other.

The whole system can be safely inertized by CO_2 formation, thanks to the layout of the waste gas passages, which was specially designed to take account of gas flow characteristics.

To obtain an indication of the risk of explosions in the waste gas system, researchers measured the expansion of the ignition area as a function of increasing hydrogen contents. It was found that the maximum admissible ratio of hydrogen to carbon monoxide, from the point of view of safety, was 0.11 (H_2 to $\text{CO} = 0.11$). The system has been in use for several years and this limit has proved to be reliable.

The tests carried out indicate that there is a certain danger of the slag becoming enriched with oxygen, especially with the LD-AC process. This can happen when ignition is retarded during the first blow, for example by floating scrap.

Retardation of ignition cannot be adequately monitored by gauging the slag viscosity. It is possible to gauge slag viscosity by measuring the attenuation of the blowing noise in the slag, but this is not a suitable method for early detection of oxygen bubbles in the slag.

Studies of the composition of waste gas, especially at the beginning and end of blowing, showed that with careful control of the oxygen blast and simultaneous monitoring of the gas composition, the volume of inert gas formed in the spent gases from the converter is sufficient to make external inertization superfluous.

The system developed and studied in this research project corresponds to the Krupp 'minimum gas' process with constant aspiration volume. The time required for the total volume of waste gas to pass through the system after the end of blowing must be measured individually for each plant, as the exact purge time for the gas system depends on the layout.

Adequate facilities must be provided for purging the system in the event of sudden ventilation breakdowns (power cuts, failure of motors, rupture of shafts or similar breakdowns). Good results have been obtained by using a steam-driven ejector mounted in the discharge stack after the electrostatic precipitator.

It is impossible to prevent dust deposits collecting in the gas system. They occur wherever the flow velocity of the dust laden gas

drops below the deposition speed of the dust fraction it contains, and wherever there are localized eddies.

Localized eddy formations can be prevented, to a large extent, by designing the layout of the gas system to take account of gas flow behaviour. Although dust fallout can occur at certain points owing to fractional retardation of the flow velocity, its effect is to reduce the flow cross-section, thus causing an increase in flow velocity.

It would appear, from observations in the research project, that this phenomenon ceases spontaneously after the fallout of a certain amount of dust, and that a certain equilibrium is established so that operation of the system is unimpaired.

Laboratory tests of the ignitability of various gas mixtures were dispensed with, as studies had shown that the simultaneous presence of oxygen and combustible gases (CO and H₂ in the gas system beyond the waste heat boiler could be avoided.

It was not possible to carry out the scheduled study of the explosion limits of various gas combinations in relation to pressure and dust content, as there was no reliable equipment suitable for this purpose.

The way in which the explosion limits vary with the gas composition was illustrated, but it was not possible to determine explosion limits as a function of pressure and dust content.

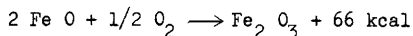
The research workers also studied the ignitability of the waste gas at the stack flare in relation to the CO content. The lower ignition limit coincided with a waste-gas loading of 345 g water/nm³ and 18% CO. The steam content corresponds to a dew point of 70°C.

Occasional incandescence of the dust deposits in the gas system was observed, and it was, quite reasonably, assumed that this phenomenon was due to pyrophoric properties of the dust.

Laboratory tests on a total of 17 dust samples showed that the average composition was as follows :

total Fe	Fe	P	Si O ₂	Ca O
47.7%	24.5 %	0.3 %	1.6 %	23.7 %

Pyrophoric behaviour results from the exothermic reactions of ferrous (iron II) oxide with oxygen as follows



On average the dust samples contained 30% ferrous (iron II) oxide

Ignition tests showed that there was a clear relationship between oxidation and the ambient temperature.

At 100° C there was virtually no oxygen absorption, but at 300° C there was a weight increase of 0.5% and at 500° C a weight increase of 1.5% was observed. These experiments showed that the dust, when exposed to air, only begins to absorb oxygen at 300° C.

The temperature in the electrostatic filter is in the region of 200° C. The slightly pyrophoric nature of the dust does not affect the evacuation and transport characteristics of the dust.

The transport characteristics and subsequent utilisation of the dust depend very much on the point at which the dust is collected. Coarser dusts and large sintered lumps collect in the bag between the stabiliser and the electrostatic filter, and this dust has a very low wettability. It is not possible to re-use this dust because it contains so many large lumps, and the material removed from the bags is dumped. The dust from the electrostatic precipitator also has low wettability and it is therefore unnecessary to monitor the moisture content.

Possibilities for recycling the dust collected downstream of the converter were investigated in a number of tests at other steelworks. It was found that returning the dust directly to the converter was not worthwhile. At present, charging the converted dust in a sinter plant appears to be the best way of making use of its high Fe content.

Dust extraction from brown fume in a Kaldo melting shop with a combination of low pressure drop venturi scrubbers and electrostatic precipitation at high flow speeds

(Société des Acières de Lorraine, Sacilor, Gandrange, Study FS 220)

The waste gases given off by Kaldo furnaces contain the same kind of pollutants as waste gases from LD and LD-AC converters. In this project a new dust extraction process, which combines the known techniques of wet scrubbing and electrostatic precipitation in a completely new way, was tested on an industrial scale.

The dust extraction plant is a wet cleaning system in four stages :

- a preliminary dust separator (prégranivore)
- a coarse dust separator (granivore)
- a multi-venturi scrubber (solivore)
- an electrostatic fine-dust precipitator.

The electrostatic fine-dust precipitator operates as follows :

1. The individual dust particles are wetted by steam.
2. The wetted dust particles are drawn into a strongly-ionized electric field together with the waste gas and thus become electrically charged.
3. The electrically charged particles are precipitated onto water droplets sprayed in in the opposite direction.

The main features of this process are therefore

- electric charging at high flow velocities (up to 70 m/s)
- precipitation of the dust in sprayed water droplets which are charged by polarization.

The main advantages of the process are :

- it is more compact than other dust extraction processes

- relatively low initial outlay and running costs
- high efficiency.

The efficiency of the dust extraction process was studied in two separate measurement periods. Two different measurement techniques were used :

1. An IKOR device

This device measures continuously and uses electrical contact interactions between the dusty gas and a contact electrode. The measurement result depends on the type of dust (chemical composition and grain size distribution), the temperature of the gas and the flow volume passing through the measurement device. As it is not always possible to keep these quantities constant, measurements with IKOR probes are used primarily for relative studies.

2. A gravimetric dust measurement process (IOY probe) was used to obtain values averaged over the whole of a melt or over the period of maximum oxygen input.

A fraction is drawn off from the stream of waste gas, the dust it contains is impinged onto a filter and the weight of the dust is measured.

Measurements by this gravimetric method were carried out over a total of 15 melts.

During the main blowing period (maximum oxygen input) the average level of the (wet) dust concentration was between 120 and 170 mg/nm^3 . The average value over a whole melt was between 50 and 100 mg/nm^3 (wet).

The relative measurements with the IKOR probe showed that the dust content fluctuated widely during the melt. The majority of the measurements indicated that the average (wet) dust concentration during the main blowing period was below 150 mg/nm^3 .

It was not possible, with the limited number of measurements taken, to determine what effect the oxygen blast and the steam content of the waste gas had on the findings.

All in all, it was found that although the dust content of the waste gas was kept within the regulation limits for the plant concerned, the gas-cleaning system did not achieve the dust-removal levels (roughly equivalent to the concentrations on the clean gas side of fabric filters) which had been anticipated following the results of preliminary tests.

Dust extraction from waste gases in open-hearth furnaces working with high scrap ratios
Thyssen Edelstahlwerke, Werk Witten, Study PS 242)

So far all of the three dust extraction methods available - wet scrubbers, dry mechanical dust collectors and electrostatic filters - have been used for dust extraction from waste gases in open hearth furnaces. All three processes have their own specific drawbacks :

- Wet scrubbers

Because of the high pressure differential required in venturi scrubbers, power consumption is high, and the treatment and disposal of effluents and slurry is extremely costly.

- Cloth filters

The standard filter material has low temperature resistance and poor mechanical strength, which creates difficulties when (as here) the operating temperatures have to be high because of the acid dew point of the waste gases processed. At operating temperatures below the acid dew point the filter material and dust evacuation systems may become clogged and caked.

- Electrostatic filters

Even with multi-phase systems it is often impossible to obtain high extraction ratios with certain types of dust, owing to the poor ionizability of the particles.

The aim of this study was, firstly, to decide by means of intensive tests which dust extraction method was most satisfactory, taking both technical and economic factors into account.

Secondly, a dust extraction system based on this method was built for a 110 t open-hearth furnace with a downstream waste heat boiler.

The researchers tried to ensure that the results were as representative as possible of all open-hearth furnaces working with high scrap ratios, as this type of furnace will continue to be used for some time.

Of the dust extraction processes mentioned above, only cloth filters and electrostatic filters were studied in this research project, as wet scrubbing is not economically feasible. The tests showed that under certain operating conditions the acid dew point may rise to 190°C . This considerably restricts the applicability of cloth filters, and the use of fibre-glass filters for open hearth furnace systems is out of the question because of the possible presence of dusts containing fluorine.

The findings indicate (cf. PS 215) that of the filter systems available, only electric filters are really suitable for open-hearth furnaces working with high scrap ratios.

The dust measurements showed dust levels of max. 27 g/nm^3 in the waste gas from the open-hearth furnace, under unfavourable conditions; to stay below the stipulated clean-gas dust level of 150 mg/nm^3 , the filter efficiency must therefore be not lower than 99.4%.

If scrap containing fluorine is charged, the concentrations of fluorine in the waste gas may be up to 2 mg/nm^3 . If fluorspar is used as a flux, the fluorine content may even be as high as 33 mg/nm^3 .

The dust is highly hygroscopic - moisture absorption of up to 25% was observed - and the dust evacuation system must therefore be specially designed to take account of this.

In line with the findings of the preliminary tests, the open-hearth furnaces were equipped with an electrostatic filter system. In the first tests carried out after commissioning of the filter system, the levels of hydrocarbons in the waste gas were measured.

Averaged over the whole period of the melt, measurements showed only traces of gaseous hydrocarbons and solid organic components (maximum value - 2.8 mg/nm³). It may therefore be concluded that the level of hydrocarbons and organic components is insignificant, as far as safety is concerned, if the fuel oil is burnt with an air factor of $\lambda \geq 1.1$.

It was found that the best temperature for dust precipitation was between 350 and 400°C, i.e. in the range of "dry" operation.

In the next part of the research project a number of different factors affecting filter efficiency will be studied in practical in-plant tests.

Development of technically and economically optimal processes for ventilation and dust extraction in steelworks shops

(Betriebsforschungsinstitut des Vereins Deutscher Eisenhüttenleute, - Düsseldorf, Study PS 224)

In order to improve the environmental conditions in the vicinity of industrial production shops and to avoid high working-place exposure to dust, toxic gases and heat, the waste gases from processes other than metallurgical ones must also be collected.

Whereas the volume of air and fumes drawn into a direct dedusting unit have to be kept down, to guarantee good dedusting by the filter unit, very large volumes of air have to be drawn off by extraction systems for enclosed spaces, owing to the need for constant ventilation. To optimize the volume flow ratios of direct extraction systems and extraction systems for enclosed spaces, the design and size of systems for pollutant collection at source and those for roof collection in shops must be compatible with each other (depending on the production sequence).

In this research project tests were carried out in electric steel works, as particularly difficult problems of pollutant propagation and ventilation are encountered in works of this type.

Measurements were taken at a large number of measurement points in the shops (at working places and just below the roof of the shop) to record air flow speeds, air temperatures and dust and pollutant concentrations.

The main contributory factors to be taken into account are the external weather conditions, the heat generated in the shop, the design of the shop and the location of dust sources in the shop. Together with these in-plant measurements, tests were carried out on models of shops, to determine the part played by individual parameters and to study the effects of design changes.

The aim of the work is to find technically and economically optimal solutions for direct extraction and secondary extraction in shops at steel works, to be implemented in new buildings and in old shops that are being renovated.

The flow dynamics characteristics of various types of extraction hood were studied in water and wind tunnels.

Air flow processes and patterns during the charging and tapping of electric furnaces were studied using a "hot model".

The findings of the model tests were put into practice in some initial designs for collection hoods.

In two electric steel works an air shield unit was installed near the tapping spout; this diverts the gases rising from the ladle during tapping so that they are drawn into a collection hood. A wide range of air and gas flow studies still in progress will provide information on optimal design and operation parameters for shield units of this kind.

Removal of the solvents in the waste air from strip-coating plants
(Stahlwerke Peine-Salzgitter AG, Salzgitter, Study PS 212)

This research project dealt with the waste air cleaning plants which had been installed downstream of the paint-drying ovens at a strip-coating plant to comply with legislation to restrict air pollution.

To keep the running costs of these plants as low as possible, a combustion system using heterogeneous catalysis was used. For the same reason, part of the cleaned air was returned to the continuous drying ovens.

The purpose of the study was to provide an answer to certain questions as to the practicability of this process:

1. How large can the quantity of recirculated air be, without the H_2O and CO_2 concentrations in the drying oven having a damaging effect on the surface quality of the coated strip?

Because the degree of conversion in the plant for catalytic afterburning was generally poor, air was only returned to the ovens when the efficiency of the afterburning process was shown to be above approximately 90%. It was important to prevent too high an accumulation of solvents in the oven. When 40% of the cleaned air was returned to the ovens the H_2O and CO_2 concentrations were not more than 1.1% and 0.7% respectively, and with these levels there was no apparent impairment of surface quality. However, the oven temperatures had to be reduced by approximately $10^{\circ}C$ compared with operation without air feedback, mainly because of the higher levels of CO_2 and hydrogen in the air jets.

2. What is the maximum amount of air that can be returned to the ovens, bearing in mind the effects of the various adhesives and solvents used, faulty operation of the afterburning system and the time lag of the measurement and control systems, without there being any danger of explosions?

This point could not be investigated owing to the generally unsatisfactory performance of the catalysts.

3. How efficient is the proposed regulation method in practice, and how must it be developed further to make it as economical and reliable as possible?

It was found that the oven-plus-afterburning system functioned best when the sequence was interrupted as little as possible by regulation and adjustments. Ideally, the volume and temperature of the air returned to the various oven zones should be constant.

4. How efficient is the proposed system for regulating the oven pressure and how must it be developed further to prevent solvents escaping from the oven into the shop?

The system originally designed for automatic adjustment of air volumes by pressure regulation in the oven was unsatisfactory. It is not possible to maintain the air volume at a given level without considerable technical facilities (computerization). The ovens should be set at medium temperatures and some means should be provided to compensate for certain fluctuations under extreme conditions.

5. In what form and quantity are paint stabilizers found in the waste air, and do they poison the catalysts?

Various components are given off into the waste gas during drying, such as binders, pigments, plasticizers and matting agents, primarily in the form of phthalates, fatty carboxylic acids, phenol derivatives and hydrochloric acid. Reaction products of these substances, heavy metal compounds and compounds containing silicon, arsenic and sulphur, have been found in the catalyst. Although these substances were traced in the spent catalyst, sometimes having undergone chemical changes, it was never possible, in reaction tests, to prove that the activity of the catalyst had been reduced and the reason for this is still not clear. It would appear that the activity measurements using propane did not provide a representative indication of the conversion behaviour of the solvents used.

6. How do the explosion limits vary with different adhesives and solvents in relation to the temperature and the concentrations of H_2O and CO_2 ?

The solvent composition of many different paint systems was measured and the lower ignition limits of the solvent mixtures were calculated. At room temperature they were between 1.49 and 0.82%. By raising the temperature to 300° C or 400° C respectively, the lower explosion limit is reduced by approximately 30 or 40% of the room temperature values.

The inevitable conclusion of this study was that under the present circumstances, satisfactory results could not be obtained in the foreseeable future with a system using catalytic afterburning. The works was therefore equipped with a conventional afterburning system.

Development of a system acceptable to welders for removal of the fumes generated by welding in enclosed spaces

(Directoraat-General van de Arbeid, Voorburg, Study PS 177)

Electric welding in enclosed areas is known to cause great discomfort for welders because of the fumes generated, especially during welding of steel plates coated with zinc primers to protect them from corrosion.

The aim of this study was to develop systems capable of extracting welding fumes without great financial outlay and with minimal inconvenience to welders. As part of the project, tests were carried out at various working places :

- at welders' working places in a workshop
- during welding of steel pipelines
- during welding in enclosed spaces, e.g. in the construction of ship sections.

The studies showed that in most cases the best results are obtained with relatively compact, portable extraction equipment.

It was shown that with the extraction equipment dust levels in the welder's ambient air could be reduced from 210-180 mg/m³ to 3-4 mg/m³. In particularly favourable conditions it was even possible to reduce the dust concentration to a level below the detection limit.

Unlike the extraction hoods originally used, which had an air aspiration rate of $38 \text{ m}^3/\text{min}$, the newly-developed portable extraction devices have an extraction rate of $7.5 \text{ m}^3/\text{min}$, so that apart from giving better extraction of dust from the welding area, they are also cheaper to run.

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
(Verein Deutscher Eisenhüttenleute, Düsseldorf, Study PS 226)

The formation of certain noxious or toxic products of combustion, such as dust or SO_2 , can be controlled by careful selection of fuels, but this is not true of nitrogen oxides which are formed in virtually all combustion processes regardless of the fuel used.

The thermodynamic processes responsible for the formation and decomposition of the nitrogen oxides NO and NO_2 are largely understood, and research has also been carried out on the main factors influencing combustion, such as temperature, partial pressure of nitrogen and oxygen, and the reaction speeds of oxide formation and decomposition, or of further oxidation.

Hitherto it had rarely been possible to apply this knowledge to practical operating conditions in the iron and steel industry, especially in industrial heating and heat treatment furnaces.

The aim of this project is to carry out pilot plant tests and tests on operational furnaces in the steel industry to study NO_x formation in relation to burner performance, gas/air ratios, preliminary gas and air pressure and furnace temperature, with a view to improving standard types of burners or developing modified burners which produce waste gases low in nitrogen oxides, without impairing, burner performance or heat transfer from the flame to the material heated.

In the work done so far, tests have been carried out on an experimental furnace with a burner using premixed natural gas and cold air.

The NO_x levels were studied in relation to the

- burner output (40 - 200%)
- air factor ($0.8 < \lambda < 1.9$), and
- wall temperature (520 - 850°C).

The measurements obtained so far indicate that the nitrogen oxide concentration increases with the wall temperature and reaches a maximum with near-stoichiometric combustion. Further experiments will show whether this is the case with other types of burner and will also provide information on the effect of pre-heating the combustion air.

Investigations into the catalytic decomposition of nitrous oxides in waste gases from metallurgical combustion processes

(Technische Hochschule, Aachen, Study PS 227)

If technical measures are to be developed capable of reducing the emission of toxic gases from metallurgical plants, the study of the reactions of nitrous oxide with alkaline and alkaline-earth oxides is of some interest. In the present research project the reactions of NO to Na_2O and CaO were therefore investigated experimentally as model cases.

The isotherms recorded by volume/pressure measurements by means of absorption apparatus and the results of the gravimetric measurements in the fluid gaseous phase show that NO is largely adsorbed by or chemically converted to Na_2O at temperatures below or above 50° C respectively. The chemical conversion of NO to Na_2O , which is facilitated by thermal dynamic equilibrium conditions, leads to the formation of various Na-O-N compounds, depending on temperature and NO- and O_2 - pressure. The exchanges are comparable with those occurring during SO_2 sorption by CaO, MgO, etc., which is used in practice for desulphurizing waste gas.

In order to illustrate the chronology of the conversion of NO to Na_2O , a kinetic model, supported by the experimental results, is being developed, taking account of adsorption, the chemical reactions and the effects of surface film formation.

According to the gravimetric experiments with CaO, which is regarded as a catalyst for NO decomposition, NO is chemisorbed by CaO, producing smaller exchanges than in the case of Na_2O ; N_2 and O_2 , which technically are the desired products of NO decomposition, are adsorbed by CaO. As with NO chemisorption, the maximum coating decreases with increasing gas-flow speed in the case of adsorption of N_2 and O_2 .

An important result of the research is the indication of the formation of N-O clusters, the kinetics and reactions of which will be studied in a further project with the help of high-vacuum apparatus which makes it possible to analyse both the gaseous phase and the products at the solid surface.

CHAPTER IVINVESTIGATION AND DEVELOPMENT OF PROCESSESFOR UTILISATION OR NON-POLLUTING REMOVALOF RESIDUES AND WASTESInvestigation on the treatment and processing of waste matter from iron and steel works(Verein Deutscher Eisenhüttenleute, Düsseldorf, Study PS 225)

In the steel industry approximately 100 kg of residual and waste matter are produced for each tonne of crude steel and the recycling of these substances presents considerable difficulties. For example, an integrated works with a crude steel output of 500 000-600 000 t/month generates the following waste :

- sludge from wet scrubbing of dust laden gas from BOS converters	approx. 4 800 t/month
- fine mill scale	approx. 12 000 t/month
- mill scale with high oil content	approx. 1 080 t/month
- other rolling waste	approx. 300 t/month
- dust from BF gas cleaning	approx. 3 900 t/month
- dust from dedusting in sinter plant	approx. 720 t/month
- dust from dust removal plant for electric furnaces	approx. 150 t/month
- iron II-sulphateheptahydrate	approx. 800 t/month
- very fine-grain iron oxide from hydrochloric acid regeneration	approx. 450 t/month

This amounts to a total of 50 700 t waste/month, and recycling or disposal of this waste presents considerable difficulties.

The aim of this research project is to reduce the amount of waste which has to be disposed of, to prevent possible effects on ground water, to reduce air pollution by waste gas from sintering and pig iron production and to minimize the effects of weather conditions on dumps and deposits of fine-grain dusts.

This entails separating the harmful substances out of the residual and waste products, especially dust and sludge. The physical properties of the cleaned waste must also be changed to permit re-use in steelmaking processes.

The substances extracted which are unsuitable for use in steel-making and damaging to the environment should be processed for other uses or rendered harmless. Recovering useful substances from the waste can help to reduce the costs of waste disposal which have to be borne by the steel industry.

Earlier studies have shown that fairly satisfactory results can be obtained by 'leaching' zinc and lead out of blast furnace sludge and dust with a number of extraction agents.

The best method appears to be a system of sludge and dust extraction in two stages.

Relatively high concentrations of zinc or lead can be obtained by using cascade extraction in each of the stages.

In the next part of the research project, experiments were carried out using the process of reverse osmosis for further processing of these extracts, to increase the zinc and lead concentrations and separate out undesirable accompanying products.

In a series of large-scale tests at a rolling mill furnace, the reducing volatilization of zinc and lead was studied. The feed mix of BF flue sludge and dry LD dust was prepared mechanically and charged into the furnace in granulated form. Approximately 5 000 t of the feed

material, which contained up to 2% lead and 4.6% zinc, was processed, and it was found that the zinc content could be reduced to 0.05% and the lead content to 0.03%. Most of the iron in the feed mix was metallized. Further experiments will be carried out to improve the consistency of the discharge so that the material can be directly charged into blast furnaces.

Study on the reduction of the zinc and lead content of materials in the production of pig iron in order to eliminate air and water pollution (ARBED, Luxembourg and CEBEDEAU, Liège, Study PS 235)

The sludge and dusts formed in the production of pig iron contain large amounts of zinc and lead. Because of these high zinc and lead contents, the sludge and dust cannot be returned to the raw materials cycle, as zinc and lead would accumulate there, nor can they be safely dumped.

The aim of this research project was to remove zinc and lead from sludge and dust so that the latter can be dumped easily. Ideally, zinc and lead should be recovered in a form suitable for use as a raw material in non-ferrous metallurgy.

Basically, two processes are considered :

- dry processes (reduction and chlorination tests)
- wet (chemical) processes.

To clean the sludge, a process consisting of the following stages was investigated:

- Leaching with NaOH

This process separates out zinc, lead and a certain amount of silicon.

- Removal of lead by cementation, using zinc powder.

- Electrolytic extraction of zinc and regeneration of the caustic soda solution.

The process has proved to be technically viable. The zinc concentrations were reduced to 10% of the original values and the lead concentrations to 25% of the original levels; but these figures are simply intended as an indication of the sort of performance that can be achieved. Under optimal conditions it would certainly be possible to obtain even better results.

The removal of silicon, one of the components of the sludge, by the caustic soda solution is fairly slow. None of the other accompanying substances of zinc and lead were found in the solutions, and this is a point in favour of the process studied, as the separation of other substances leads to unnecessary consumption of reaction chemicals. Only silicon is found as an impurity in the NaOH and it is economically feasible to regenerate the solution by the addition of $\text{Ca}(\text{OH})_2$, so that the silicon is precipitated out in the form of calcium silicate.

The main difficulty encountered in the course of the tests arose from the grain size of the solids treated. These solids are in the form of very fine particles which are difficult to sediment and also clog the filters very quickly. The difficulties were overcome by centrifuging of the mixture of solid and liquid constituents. It would also be possible to coagulate the lixiviated sludge.

The leaching process did not present any particular problems. Good results are obtained and most of the lead in the sludge can be recovered.

Electrolytic extraction of the zinc is feasible, given good conditions, but the results are always dependent on the cleanliness of the electrolyte and preliminary cleaning is therefore necessary. Since the solutions treated are not very concentrated, low voltages must be used, with large electrode surfaces and strong agitation of the bath fluid.

The general results of the laboratory tests were good enough for the research to be continued on a pilot plant.

It became clear from findings obtained in conjunction with another research project (PS 225) that the process of dry chlorination was not suitable for dusts with high carbon contents (such as dusts and sludge from pig iron production).

Research work on this topic has therefore been abandoned.

Recovery of valuable materials from sludge produced during the re-treatment of blast furnace waste gases
Laboratoires de Réfractaires et Minerais, Nancy, Study PS 258)

The sludge resulting from the re-treatment of blast furnace waste gases, amounting to 2 to 3 kg of dry matter per tonne of hematite pig iron and 5 kg per tonne of phosphorus pig iron, consists of blast furnace charging materials (iron ore and partially reduced sinter, coke, etc.) and non-ferrous metals such as zinc and lead which are found in concentrated form. As the zinc content is from 5 to 25% and the lead content from 1 to 9%, the sludge may be considered as an ore rich in zinc and lead. Sludge treatment aimed at recovering these costly metals is of great economic importance and will lead to reduced environmental pollution, particularly of the ground water below slag heaps. The purpose of this research is to develop technically and economically viable procedures in order to achieve the following results :

- No more dumping of sludge on slag heaps.
- No more pollution of ground water.
- Recovery of zinc and lead which are now becoming scarce and rapidly rising in price.
- Recycling of the residues - i.e. iron ore and coke.

With this in mind, it is intended to carry out the following work :

- The taking of sludge samples from blast furnaces for hematite and phosphorus pig iron.
- Investigation of the phases present (degree of oxidation and proportions of zinc and lead).
- Granulometric analysis.
- Sludge treatment by selective flocculation, flotation by means of carrier minerals and wet high- and low-current magnetic separation.
- Oxidation-reduction treatment for the selective reduction of zinc and lead oxides.

So far, tests have been carried out on four zinc- and lead-containing sludge samples taken from phosphorus pig iron blast furnaces. Analysis has shown considerable differences between samples.

The zinc content ranged from 3.3 to 13%
and the lead content from 1.44 to 3.6%.

Investigation of the proportion of zinc present in the various phases produced the following results :

- In the crude product (sludge sample in its original composition) :
Zinc in the form of zinc oxides and zinc hydroxides amounted to 65 to 75% of the total zinc content.
Zinc in the form of ZnS (wurtzite) and silicates amounted to 10 to 16%.
Zinc in the form of ferrous compounds amounted to 14 to 16%.
- In the grain fraction $< 10 \mu$, the percentages were as follows :
Zinc oxides and zinc hydroxides 40 to 65%.
ZnS and silicates 30 to 45%.
Zinc in ferrous compounds 16 to 18%.

Comparison of these results shows that in passing from crude sludge to the fraction $<10 \mu$, the ratio

$$\frac{\text{Zns + Silicates}}{\text{Total Zn}}$$

increases by the factor 3. The zinc content can therefore be enriched by means of granulometric separation.

Approximately the same values can be attained for the enrichment of lead.

In addition, a grain size fraction of $>500 \mu$ was determined. This is to be further examined under an electron microscope since it can amount to as much as 3% by weight of the crude sludge and contain as much as 4% of the total Zn content.

The remaining work consists of attempting the selective separation of metallic Zn and wurtzite (ZnS). Further experiments are being conducted in order to enrich the samples examined so far. Finally, size reduction experiments are in hand with the grain size fraction $37 - 104 \mu$.

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

(Centre Belge d'Etude et de Documentation des Eaux, Liège + Centre de Recherches Métallurgiques, Liège. Study PS 236)

The aim of the research work was to devise equipment for the purpose of destroying mill oils by combustion, using burners specially adapted for controlled regulation of combustion.

The study is in three parts :

- Analysis of the used oils to determine the following:
 - percentage of free oil
 - percentage of emulsified oil
 - suspended matter other than oils

- acidity
- stability of the emulsion
- polarity
- Study of the separation and breakdown of the emulsions by
 - electrostatic flotation
 - breakdown by de-emulsifiers
- Combustion tests.

An initial series of tests dealt with the treatment of residues from the oil sump by centrifugation.

Under optimal operating conditions it was possible to recover an oil with a water content of less than 12%, and sludge containing 20 to 40% oil-containing constituents and 20% water.

In the second series of tests, residues from the circulation tank skimmers were studied. The mixture was centrifuges to remove the solid components and separate the oil and other liquid from each other.

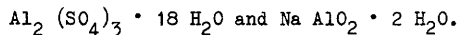
The results obtained were remarkable in respect of :

- the dryness of the sludge
- the quality of the oil recovered (water content and ash content)
- the carrier liquid (emulsion medium) could be recirculated.

Tests on the breakdown of emulsions were carried out, using aluminium sulphate.

Soda, sodium aluminate and chalk were used for coagulation.

The best results were obtained with



At normal temperatures (30 - 35° C) coagulation was encouraged by adding 1.5 g aluminium sulphate/l, and approximately 0.8 g aluminate/l were required for neutralization. These levels can be reduced to 0.5 and 0.2 g/l respectively by heating the solution to 75°C.

In spite of the good cleaning performance of the system, the water quality is not high enough for direct discharge into the natural environment. The main problem here is the detergent content.

In a further series of tests the possibility is being investigated of adding the oily effluent to the heavy fuel oil injected into blast furnace tuyeres. The work will begin with laboratory tests and pilot plant tests to study both the combustion of the mixture and the stability of the fuel oil-plus-effluent emulsion.

1. TESTING, IMPROVEMENT AND DEVELOPMENT OF EQUIPMENT AND PROCESSES FOR DETERMINING AND MEASURING AIR POLLUTION

1	2	3	4	5
Project Reference	Research undertaken by	Subject of research	Date for commencement and completion of research	Maximum aid as % of research cost - in national currency - in u.s.a.
PS 157	Institut für Mechanische Verfahrenstechnik der Universität Karlsruhe Richard-Willstätter Allee D 75 KARLSRUHE 1	Grain analysis of dusts with grain size less than $1 \mu\text{m}$	01.12.1970 01.12.1973	26,00 % 150.000,00 DM 40.983,61 u.s.a.
PS 167	Institut National de Recherche Chimique Appliquée (IRCHA) 12, Quai Henri IV F 75004 PARIS	Application of count efficiency curves to improve the accuracy, reproducibility and comparability of dust measurement at works	01.10.1971 31.03.1972	65,00 % 92.300,00 FF 16.618,09 u.s.a.
PS 175	Instituut voor Gezondheidsstechniek T.N.O. Schoemakerstraat, 97 NL DELFT	Investigation of the effects on dust particles and of the medium in which the particles are held during counting	01.07.1971 31.12.1976	65,00 % 31.200,00 Hfl 8.618,79 u.s.a.
PS 209	Instituut voor Gezondheidsstechniek T.N.O. Schoemakerstraat, 97 NL DELFT	Determination of the size and distribution of suspended particulate in the air by holographic methods	01.01.1971 31.12.1974	65,00 % 82.550,00 Hfl 22.803,87 u.s.a.

PS 194	Institut National de Recherche Chimique Appliquée (IRCHA) 12, Quai Henri IV F 75004 PARIS	Comparative study of optical processes and sedimentation processes for determining grain size in dust samples	01.10.1971 30.10.1972	65,00 % 35.750,00 FF 6.436,59 u.a.
PS 206	Instituut voor Gezond- heids techniek T.N.O. Schoemakerstraat, 97 NL DELFT	Tests to determine the number of 0.5 - 5 μ m quartz particles in a dust sample by means of interference microscopy	01.11.1972 31.07.1976	65,00 % 39.000,00 Hfl 10.773,48 u.a.
PS 210	Instituut voor Gezond- heids techniek T.N.O. Schoemakerstraat, 97 NL DELFT	Study of the way in which the dimensions of dust par- ticles can influence the result of airborne dust measurements with an aspir- ation probe	01.04.1971 31.12.1976	65,00 % 173.550,00 Hfl 47.942,00 u.a.
PS 232	Laboratoire d'Etude et de Contrôle de l'Envi- ronnement Siderurgique Voie Romaine - B.P. 36 F' MAIZIERES-LES-METZ	Direct and non-destructive analysis of pollutants from the iron and steel industry	01.12.1972 31.05.1976	60,00 % 150.000,00 FF 27.006,64 u.a.
PS 230	Laboratoire d'Etude et de Contrôle de l'Envi- ronnement Siderurgique Voie Romaine - B.P. 36 F MAIZIERES-LES-METZ	Adjustment and calibration of systems, particularly optical ones, for the con- tinuous monitoring of dust emissions from iron and steel plants	01.12.1972 31.12.1975	60,00 % 300.000,00 FF 54.013,28 u.a.
PS 159	Betriebsforschungsinsti- tut des Vereins Deutscher Eisenhüttenleute (VDEh) Breite Strasse, 27 D 4 DUSSELDORF	Continuously recording meas- urement of the solids in gas- dust mixtures with the 'Konitest'	01.05.1969 30.09.1972	62,50 % 100.000,00 DM 27.322,40 u.a.

1	2	3	4	5
PS 231	Laboratoire d'Etude et de Contrôle de l'Envi- ronnement Chimique Voie Romaine - B.P. 36 F 91410-LEPES-LEZ-NETZ	Development of a method of analysing measurements of atmospheric pollution in the iron and steel industry	01.01.1975 31.03.1975	60,00 % 930.000,00 FF 173.167,40 u.s.a.
PS 216	Laboratorio di Igiene Industriale della Clinica del Lavoro dell'Università di Milano Via San Barnaba, 8 I 20122 MILANO	Measurement of fluorine in emissions from iron and steelworks with the Orion Research Inc. specific fluorine ion analysis electrode	01.11.1970 31.10.1972	59,80 % 5.500.000,00 Lit. 8.800,00 u.s.a.

II. MEASUREMENT OF AIR POLLUTION AT WORKPLACES
AND IN THE IMMEDIATE VICINITY OF STEELWORKS

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 national currency - in u.s.
PS 140	Centre Belge d'Etude et de Documentation des Eaux (CEBDEFAU) 2, rue Armand Stévert B 4000 LIÈGE	Systematic determination of different air pollutants from a coking plant in an iron and steel works complex	01.09.1969 30.10.1972	60,00 % 3.582.000,00 FF 71.640,00 u.s.
PS 240	Centre d'Etudes et de Recherches des Charbonnages de France (CERCIAP) 33, rue de la Baume F 75008 PARIS	Controlling dust extraction from charging emissions where preheated coal mixes are used	01.08.1974 31.07.1976	60,00 % 300.000,00 FF 57.473,35 u.s.
PS 158	Bayerisches Landesinstitut für Arbeitsschutz Pfererstrasse, 3 D 8000 München 20	Continuously recording measurement of dust levels in iron and steel works with the identification and measurement of the toxicity of certain dust samples	01.09.1971 31.08.1978	75,00 % 120.000,00 DM 32.786,08 u.s.
PS 169	Staubforschungsinstitut des Hauptverbandes der gewerblichen Berufsgenossenschaften Lenzwarder, 103 D 53 501N	Determining the concentration of silicometric, toxic and other noxious dust at working places in the iron and steel industry	01.07.1970 30.06.1974	41,45 % 80.000,00 DM 21.057,08 u.s.

1	2	3	4	5
PS 161	Laboratoire de minéralogie et de Microscopie électronique du Musée d'Histoire Naturelle Marché-aux-Poissons, 80 LUXEMBOURG	Investigation of air pollution at different places of work in Luxembourg iron and steel works and in their immediate environment	01.08.1969 31.08.1973	53,57 % 1.350.000,00 Flux 27.000,00 u.a.
PS 176	Instituut voor Gezondheids- heidstechniek T.N.O. Schoemakerstraat, 97 NL DELFT	Investigation of the distribution of air pollutants in workshops by air currents arising from heat, draughts and fans	01.09.1970 28.02.1974	29,55 % 72.400,00 Hfl 20.000,00 u.a.
PS 179	Istituto di Igiene dell'Università di Genova Via Pastore, 1 I 16121 GENOVA	Experimental investigation into the dispersion pattern of a number of air pollutants (sedimentary dust, suspended dust and sulphurous waste gases) emanating from the iron and steel industry	01.01.1972 01.01.1976	22,40 % 6.250.000,00 Lit. 10.000,00 u.a.
PS 204	Betriebsforschungsinstitut des Vereins Deutscher Eisenhüttenleute (VDh) Breite Strasse, 27 D 4 DUSSELDORF	Dust emission during loading and storage of bulk goods	01.09.1971 28.02.1976	62,50 % 175.000,00 DM 47.811,21 u.a.
PS 218	Rhein Stahl AG, Bau- und Wärmetechnik Hohenzollerstrasse, 2-4 D 465 GELSENKIRCHEN	Study of the effect of sinter plant charging and operating conditions on the dust content of sinter waste gas and the physical properties of the dust	01.03.1971 30.06.1975	65,00 % 250.000,00 DM 68.306,00 u.a.

PS 215	Betriebsforschungsinstitut des Vereins Deutscher Eisenhüttenleute (VDEh) Breite Strasse, 27 D 4 DUSSELDORF	Evaluation of the kind and quantity of emissions on operation of open-hearth furnaces in relation to the melting process	01.04.1971 30.06.1974	66,10 % 200.000,00 DM 54.644,81 u.s.a.
PS 223	Betriebsforschungsinstitut des Vereins Deutscher Eisenhüttenleute (VDEh) Breite Strasse, 27 D 4 DUSSELDORF	Causes of dust formation during surface treatment of steels by flame scarfing and grinding	01.12.1972 31.12.1975	60,00 % 297.000,00 DM 81.147,54 u.s.a.
PS 163	Institut National de Recherche Chimique Appliquée (IRCHA) 12, Quai Henri IV F 75004 PARIS	Rapid oxidation of SO ₂ to sulphuric acid in the presence of iron oxide in moist air	02.02.1969 30.09.1972	48,22 % 103.677,00 FF 18.666,45 u.s.a.
PS 238	Centre Belge d'Etude et de Documentation des Eaux (CBEDEFAU) 2, rue Armand Stévert B 4000 LIEGE	Study of the real compo- sition of fluorinated sub- stances emitted into the air from iron and steel- works, for the purpose of devising a means of con- verting toxic fluorinated compounds into less harmful substances	01.06.1975 31.05.1977	60,00 % 1.939.500,00 FF 39.860,19 u.s.a.

III. INVESTIGATION AND DEVELOPMENT OF PROCESSES FOR TRAPPING AND
PRECIPITATING AIR POLLUTION, OR FOR REDUCING THE OCCURRENCE
THEREOF

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 national currency - in u.a.
PS 237	Centre Belge d'Etude et de Documentation des Eaux (CEBEDEAU) 2, rue Armand Stévant B 4000 Liège	Purification of toxic fumes produced during slag granulation	01.05.1975 31.12.1977	60,00 % 950.500,00 FB 20.635,85 u.a.
PS 199	Stahlwerke Peine-Salzgitter AG D 522 SALZGITTER 41	Dust removal from CO-containing waste gases from oxygen blowing converters by means of electric filters	01.07.1969 30.06.1973	34,00 % 2.094.000,00 DM 572.131,15 u.a.
PS 220	Société des Aciéries de Lorraine (SACILOR) Usine de Gandrange F 57 AMNEVILLE	Dust extraction from brown fume in a Kaldo melting shop with a combination of low pressure drop Venturi scrubbers and electrostatic precipitation at high flow speeds	01.01.1972 31.12.1974	60,00 % 1.200.000,00 FF 216.053,11 u.a.
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 % 1.140.000,00 DM 373.302,94 u.a.

PS 224	Betriebsforschungs- stitut des Vereins Deutscher Eisenhütten- leute (VDÉh) Breite Strasse, 27 D 4 DÜSSELDORF	Development of technically and economically optimal processes for ventilation and dust extraction in steelworks shops	01.12.1972 31.12.1977	60,00 % 582.000,00 DM 159.016,39 u.a.
PS 212	Stahlwerke Peine- Salz- gitter AG D 332 SALZGITTER 41	Removal of the solvents in the waste air from strip-coating plants	01.02.1969 30.06.1974	42,53 % 189.000,00 DM 51.639,34 u.a.
PS 177	Directoraat-Generaal van de Arbeid Balen van Anselplein,2 NL VOORBURG	Development of a system acceptable to welders for removal of the fumes gen- erated by welding in enclosed spaces	01.10.1969 30.06.1972	61,50 % 20.000,00 Hfl 5.525,00 u.a.
PS 226	Betriebsforschungs- stitut des Vereins Deutscher Eisenhütten- leute (VDÉh) Breite Strasse, 27 D 4 DÜSSELDORF	Investigation of total nitrogen oxide emissions from industrial gas fur- naces with a view to the development of burners with waste gases having a low nitrogen oxide content	01.11.1974 31.12.1977	60,00 % 411.000,00 DM 134.585,53 u.a.
PS 227	Lehrstuhl für Metallur- gie der Kernbrennstoffe und Theoretische Hütten- kunde - Th Aachen D 51 AACHEN	Investigations into the catalytic decomposition of nitrous oxides in waste gases from metallurgical combustion processes	01.12.1972 31.12.1975	60,00 % 177.000,00 DM 48.360,66 u.a.

IV. INVESTIGATION AND DEVELOPMENT OF PROCESSES FOR
UTILISATION OF NON-POLLUTING REMOVAL OF RESIDUES
AND WASTES

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 national currency - in u.s.
PS 225	Betriebsforschungs-institut des Vereins Deutscher Eisenhüttenleute (VDIh) Breite Strasse, 27 D 4 DUSSELDORF	Investigation on the treatment and processing of waste matter from iron and steel works	01.11.1973 31.07.1977	68,34 % 1.695.000,00 DM 555.042,52 u.s.
PS 235	ARBED - Division d'Esch Belval - C.P. 142 L ESCH-SUR-ALZETTE Centre Belge d'Etude et de Documentation des Eaux (CEBEDEAU) 2, rue Armand Stévant B 4000 LIEGE	Study on 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 % 10.008.564,00 FB 242.628,25 u.s.
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 re-treatment of blast furnace waste gases	01.04.1975 30.09.1977	60,00 % 591.480,00 FF 113.314,46 u.s.

<p>FS 236</p>	<p>Centre Belge d'Etude et de Documentation des Eaux (CEEDEAU) B 4000 LIEGE</p> <p>Centre de Recherches Metallurgiques Abbaye du Val Benoît B 4000 LIEGE</p>	<p>Study of the combustion of used emulsions from cold rolling mills without air-polluting residues</p>	<p>01.01.1975 31.12.1977</p>	<p>75,00 % 5.758.000,00 FB 125.009,22 u.s.a.</p>
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Research progress report: 30th June 1977**

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