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Catalytic abatement of fugitive gaseous pollutants from iron-making processes (ENV4-CT97-0599)

*Original*

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**Nancy, France**  
**6 - 10 October 1998**  
*Palais des Congrès de Nancy &  
National Geological Engineering School of Nancy (INPL)*

Workshop co-organized by

IRH Environnement,  
the EU-funded Concerted Action on Environmental Technologies, ETCA  
the Environment and Climate Programme of the European Commission (DGXII-D1),  
& the National Geological Engineering School of Nancy (INPL)

Form *Project Contributions***Project data sheet** (*please do not exceed 2 pages*)

**Project Title:** Catalytic abatement of fugitive gaseous pollutants from iron-making processes

**Contract Number:** ENV4-CT97-0599

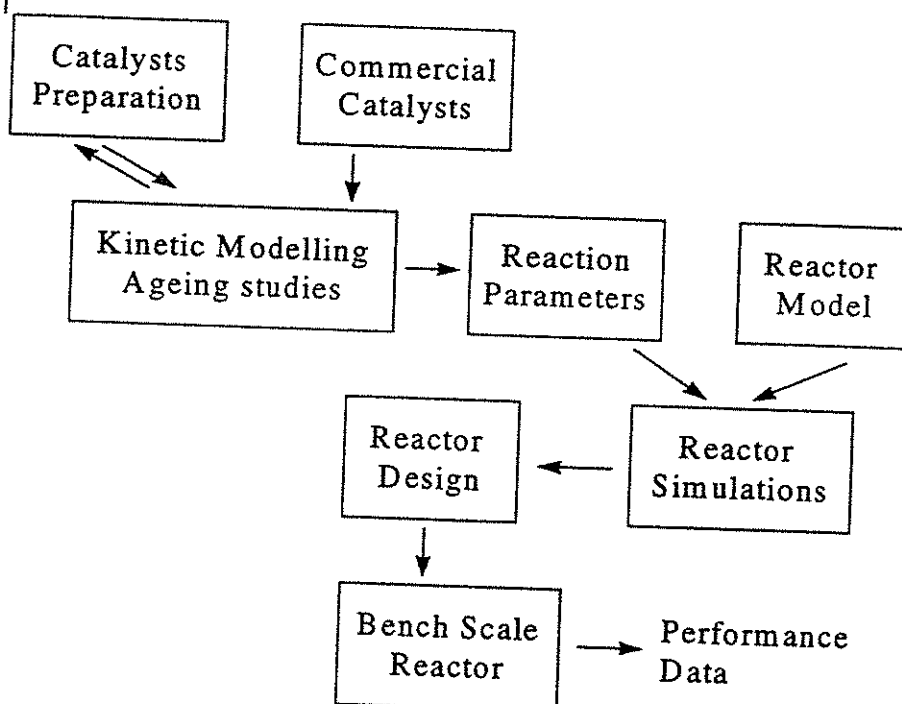
**Duration:** 36 months

**starting date:** 1/04/1998

**end of project:** 31/03/2001

**Objectives:** (*5 lines approximately*)

The main objective of this Research Project is to find the bases of an original process for the abatement of VOC gaseous pollutants from fugitive emissions of the iron- and steel-making industries. The process will be based on catalytic deep oxidation, and aims to overcome the drawbacks of currently applied technologies. It includes the design of a very robust catalyst, which must sustain broad variations in gas composition, flow rate and operating conditions, and to resist poisoning by inorganic gases, and the design of an energy-efficient reactor. The process will be tested in a bench-scale installation.

**Project technical diagram/flow sheet:****Detailed, updated co-ordinates of project co-ordinators and project partners:****Co-ordinator**

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Scientific/technical approach:

The Research Project will be developed according to four main tasks, related to the aforementioned project objectives:

- a. Preparation and characterisation of new catalytic systems, active for the deep oxidation of VOC (methane, ethane, ethylene, benzene), robust, and resistant to poisons, including systematic measurements of catalytic activity and characterisation of used catalysts.
- b. Kinetic modelling and ageing studies on specially prepared catalysts. Comparison with commercially available catalysts. Optimisation of operating parameters.

- c. Design of energy-efficient reactors for the treatment of the emissions with minimum energy consumption, by numerical simulation of the unsteady system. Evaluation of different design alternatives (reverse flow vs. network of reactors).
- d. Realisation of a bench-scale nonstationary reactor. Experimental evaluation of the reactor performances and validation of the design codes.

### Results:

At this early stage of development of the Research Project, only preliminary results are available. Samples of precious metal and mixed oxides commercial catalysts have been acquired, and some special catalysts have been prepared. The first results on their activity studies are being produced at present. In relation to the simulation studies of the non-stationary fixed-bed reactors, a complete monodimensional model, as well as a simplified model useful for optimisation and comparison of alternatives have been developed. Preliminary simulation results indicate that the stability range of a network of unsteady burners for low VOC concentration is very narrow when adopting a fixed cycle period.

### **Extended abstract of project (scientific/technical approaches, results)**

*(please do not exceed 5 pages)*

#### INTRODUCTION

Although there are technologies available for collecting and treating most of the gaseous emissions of the steel- and iron-making industries, there still exist several emissions sources for which treatment is lacking or not satisfactory. Among them, fugitive emissions that occur at coke ovens, sinter plants, blast furnaces, steel converters, and teeming, casting and rolling plants are especially important. They contain volatile organic compounds at low concentration, together with inorganic gases ( $H_2S$ ,  $NH_3$ ,  $SO_2$ ) and particulate. Because of their toxic nature, they represent a hazard for human health as well as for the environment. Although technologies for eliminating compounds such as particulate and inorganic gases are available, treatments for the abatement of VOC from such emissions at reasonable cost are lacking.

The objective of this Research Project is to establish the bases, at a pre-development stage, of a process for the abatement of pollutants from the aforementioned emissions, based on deep catalytic oxidation, and specially adapted to the specific constraints of such emissions. In order to attain this goal, the following specific objectives are to be attained:

Design and preparation of new oxide catalysts specially suited for the deep oxidation of VOC in the presence of poisons. Testing of these specially designed new catalysts (activity, kinetics, ageing, regeneration and resistance to both poisons and steam), and comparison to available commercial catalysts.

Modelling of the reaction system, and design of energy-efficient reactor in order to treat such emissions with minimum energy consumption.

Design, construction and operation of an energy-efficient catalytic bench-scale reactor for testing of catalysts at process on real industrial conditions.

#### SCIENTIFIC/TECHNICAL APPROACH

To attain these objectives, the project is divided in four tasks:

1. Preparation and characterisation of new catalytic systems, active for the deep oxidation of VOC (methane, ethane, ethylene, benzene), robust, and resistant to poisons, including systematic measurements of catalytic activity and characterisation of used catalysts.

The catalyst formulation will take advantage of the variable regime of feed and of the cycle operation of the reactor, including «reservoir» phases, which can temporarily accept poisons before they are reacted in a subsequent stage of the process. Active oxides with structures that are known to resist modifications in the presence of steam and frequent variations of temperature, will be selected.

The design of new catalysts will proceed through 3 main steps: synthesis, catalytic activity measurement, and characterisation of fresh and used catalyst samples. The systematic characterisation of used catalysts will be used in order to correlate possible catalyst modifications to variations of activity, stability and resistance to poisons.

2. Kinetic modelling and ageing studies on both especially prepared and, for the sake of comparison, commercially available catalysts. Optimisation of operating parameters.

Preliminary experiments will be carried out in a microreactor over a range of particle sizes, space velocities and temperatures, in order to determine the working regime of the catalysts, either diffusion or kinetics limited. VOC samples will be injected varying the composition of the main constituents at two levels, low and high, as required by factorial experimental designs, and at different humidity levels.

Kinetic models based on well known equations found in the literature, adapted to the complex mixtures to be used, will be fitted to the experimental results obtained in this Project. If necessary, they will be modified or new models will be developed.

The effect on catalyst deactivation on the kinetics (rate, selectivity to complete oxidation, temperature increase to maintain activity, possible formation of harmful products) will also be studied.

3. Design of energy-efficient reactors for the treatment of the emissions with minimum energy consumption, by numerical simulation of the unsteady system. Evaluation of different design alternatives (reverse flow vs. network of reactors).

The simulation of the unsteady reactors requires the solution of a system of partial differential equations in 1 or 2 dimensions, plus time, depending on the required accuracy. The adopted numerical technique consists in transforming the partial differential equations in ordinary differential equations in time by discretising the spatial co-ordinates. The ordinary differential equations can then be solved by standard integration methods. Once the reaction models and preliminary calculation tools are ready, the different alternatives for the reactor design will be evaluated and compared in order to choose the most efficient one, considering in particular the reliability and stability of the system in presence of disturbances and large variations of the load. The calculations will be carried out taking into account the results of the kinetic studies, and will lead to the design of a bench-scale reactor for the treatment of VOC emissions.

4. Realisation of a bench-scale nonstationary reactor. Experimental evaluation of the reactor performances and validation of the design codes.

The performance of the catalysts found to be the more efficient in the lab-scale studies, and the energy-efficient reactor design will be tested in a bench-scale reactor. Using these catalysts, preliminary steady-state experiments will be carried out. Particular attention will be given at this stage to the evaluation and minimisation of heat dispersions. The first results will allow refining and validating the reactor simulation model.

In a second step, the performance of the reactor will be evaluated. In particular, the control policy will be tested and optimised. The reactor will be operated under different conditions, testing the robustness of the control system and its capability to sustain periods of stand-by.

## RESULTS

At this early stage of development of the Research Project, only preliminary results are available. Samples of precious metal (Pt and Pd on alumina) and mixed oxides ( $\text{CuO}/\text{Cr}_2\text{O}_3/\text{TiO}_2$ ) commercial catalysts have been acquired, and some special catalysts have been prepared (multicomponent mixed oxide catalysts of comparatively high surface area). The experimental set-ups for catalyst testing and kinetic studies have been assembled, and first results on the studies of catalytic activity are being produced at present. Approximate values of the pseudo-first order kinetic parameters for the oxidation of methane over a commercial Pt/alumina catalyst have been calculated, and used for the simulation studies.

Corresponding to the simulation studies, a complete monodimensional model for the unsteady-state reactor has been considered. It includes three partial differential equations (one mass balance for the gas, one energy balance for the solid phase and one energy balance for the gas), one equation for the mass balance of the solid phase and one linear kinetic expression. Absence of matter storage in the solid phase and reaction limited to the outer catalyst surface have been assumed. For the solution of the model equations, space derivatives are discretized, so that the problem is reduced to a set of ordinary differential equations, that are solved through the fortran routine "LSODE" included in the "ODEPACK". A modular code has been developed that can be applied

to simulation of both reactor configurations. The program has been tested comparing the results with analytical and numerical solutions in several special cases.

The main objective of the work has been not a complete sensitivity analysis of the reactors, since this subject was investigated by many other authors previously, but the development of a fast-design methodology to be used for optimisation and comparison of different alternatives. To this purpose a lot of effort has been put into the development and validation (using the complete model) of simplified models, whenever this was possible. The adopted approach has been the consideration of analogy between the final steady state in the reverse-flow reactor and the normal steady state in a countercurrent stationary reactor, as for the adiabatic case it allows to get immediately the three main parameters of the steady temperature profile (maximum value, slopes and shift velocity). The research focused on finding the stability map (minimum  $T_{ad}$ , minimum flow rate, allowable switching-frequency range,  $T_{max}$ ) in a particular situation (combustion of low concentration of methane, typical noble-metal kinetics, laboratory-size reactor), with the purpose to extend gradually our investigation to more complex cases.

The first results obtained are summarised below.

#### Reverse-flow reactor

In the conditions of low VOC concentrations, that have been investigated, only two steady-states are possible: the ignited case, in which conversion exceeds always 99 %, and the extinguished one, with no conversion. Nevertheless, before the steady-state is attained, a transient evolution of the profiles can lead to a temporary fall of conversion, that, for the not adiabatic situation, can reach also minimum values less than 90 % for a long period (many hours). This effect can be strongly limited increasing the pre-heating temperature of the reactor. In the adiabatic case, the maximum value of the catalyst temperature is influenced by VOC concentration ( $T_{ad}$ ), flow rate, inert fraction, but not by bed length and switching frequency. If, on the contrary, we introduce a heat loss from the outer surface, also the two last factors affect the performance. In both cases, bed length and switching frequency affect the size of the hot zone. The extinction of reaction occurs in three cases: a. too low heat supply from combustion; this factor is influenced by  $T_{ad}$  and flow rate; b. too long cycle period, with the hot front getting out of the reactor; c. (for the not adiabatic condition, only) too short cycle period, that leads to an excessive extension of the hot zone, and consequently to a not bearable superficial heat dispersion.

Using the approximate model, all these observations can be converted in data and charts, that can be verified through the complete model simulations.

#### Network of unsteady burners

The most important observation about this operating way is that the stability range, when adopting a fixed cycle period, is very narrow: the stable cycle period depends on bed length,  $T_{ad}$ , flow rate; the reaction does not extinguish only if the imposed frequency is very close to that value. Besides, it takes a very long time for the system to reach a steady-state (about twice that of the reverse-flow). Therefore, it is of course necessary to apply a different control method. About this and other subjects, the work is still proceeding.

#### **Publications, patents, exploitation**