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Multiannual programme of the Joint Research Centre 1980-83

1983 Annual Status Report

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HYDROGEN PRODUCTION
ENERGY STORAGE AND TRANSPORT

1983

Research Staff (allocated): 40 men-year
Budget (allocated): 4.372.000 ECU

Projects:

1. Thermochemical Production of Hydrogen
2. Advanced Studies for Energy Carriers
3. Study of Technical Systems

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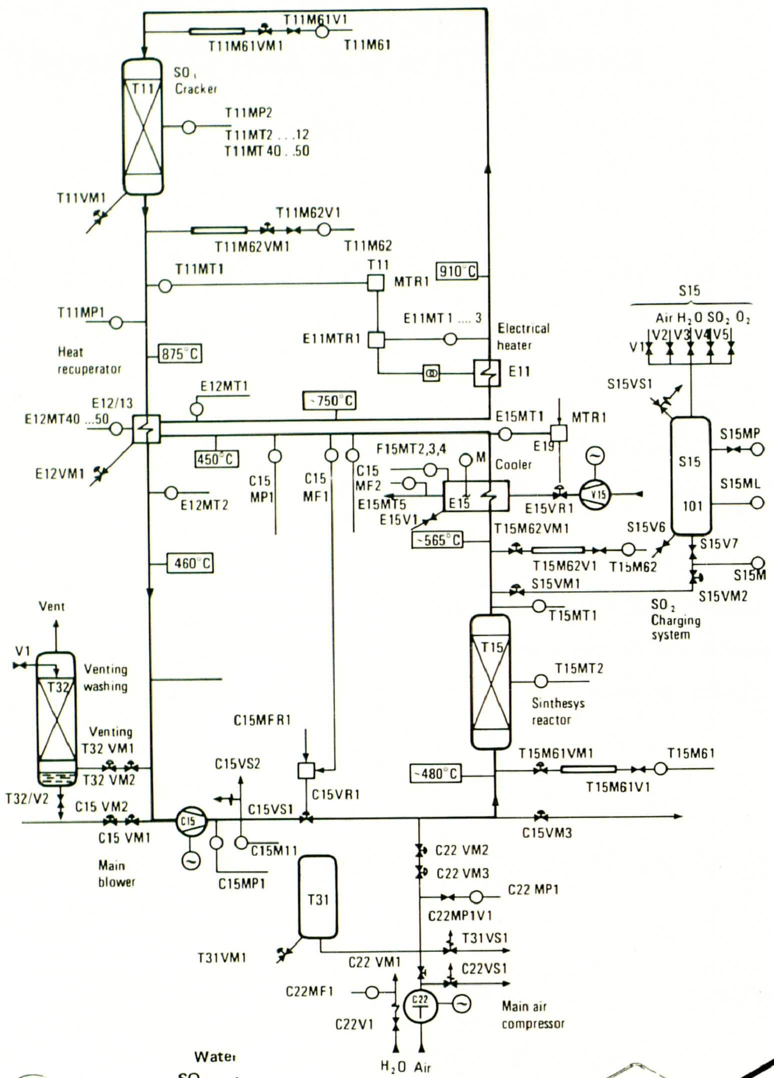
1. INTRODUCTION

In the development of new energy sources, a great deal of attention has been devoted to the sources themselves and to systems of conversion. Nevertheless, the storage and transport of the energy produced are an essential requirement for the economic utilization of the new systems, whether because of the intermittent nature of the source, or because of the mode of utilization (mobile applications), or because of the distance between the centres of production and consumption.
The cost-effectiveness of these primary energies is closely linked with the development of economic storage or transport systems.
In these respects, hydrogen holds out attractive prospects: hence the JRC's interest in the production of this energy carrier.
The experience acquired at Ispra in the previous «Hydrogen» Programme provides a solid basis for the development also of new techniques (or for the verification of known but unproven techniques) for the storage and transport of energy, especially by thermo-chemical processes.
The activities on hydrogen production, are going to a conclusion of the research phase; all the programme is progressively decreasing because the studies on energy storage and transport are no more included in the next Pluriannual Programme.
The activities are subdivided in the three following projects:

— **Thermochemical production of hydrogen.**
The experimental realizations, as a results of the previous programmes, terminate in the current multiannual programme. The objective is to verify the technological feasibility and the competitivity of the thermochemical hydrogen production route on a semi-industrial scale.

— **Advanced studies for energy carriers.**
The problem of storing and transporting energy can be solved in different ways, according to the situation and the system; an activity of exploratory nature is useful for the definition and selection of various techniques to transport and store energy.

— **Study of systems.**
The aim is an evaluation of various, possible systems for collection-conversion-transmission-storage-utilization of energy under different conditions.



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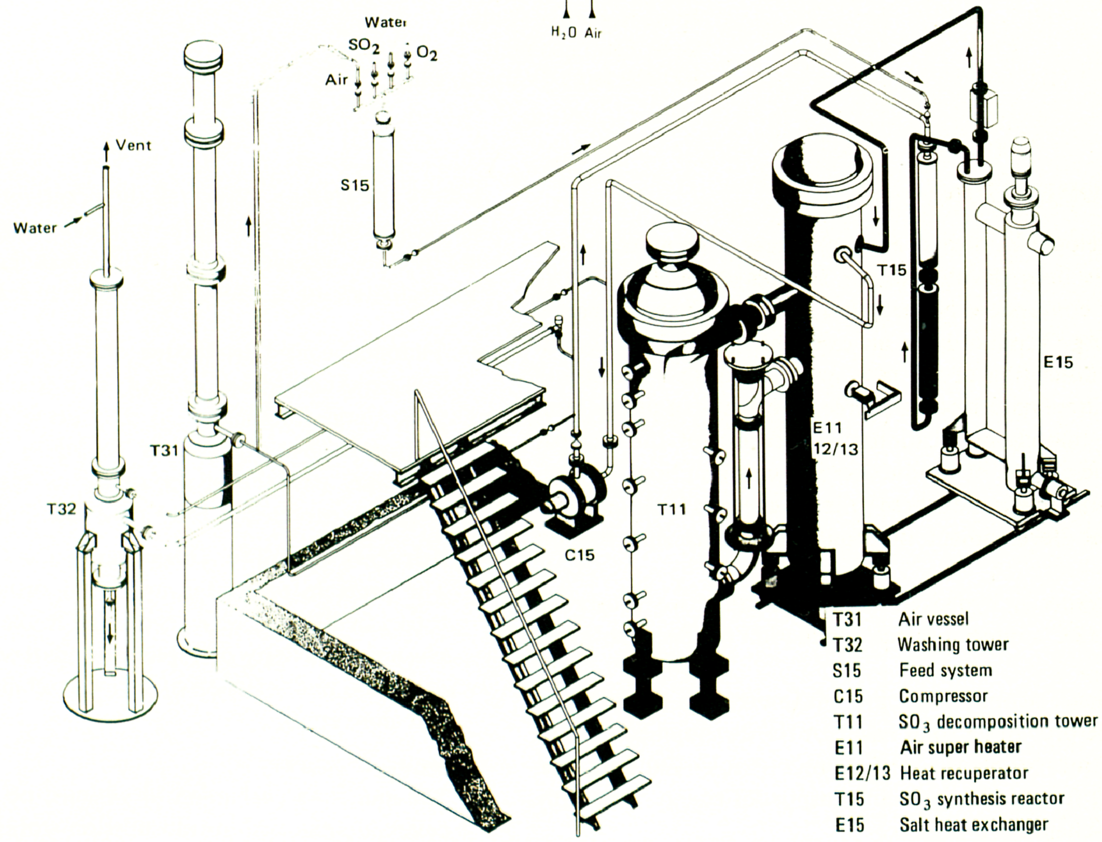

Fig. 1 and 2. The technological circuit: schemes of the loop and of the plant

2. RESULTS

Project 1. Thermochemical Production of Hydrogen

The objective of the activity is the verification of the feasibility and competitivy of the thermochemical decomposition of water, as a possible new method for hydrogen production, using high temperature heat as primary energy.
After the exploratory studies and the preliminary tests made in the past years, the research phase, concentrated on two of the cycles defined at Ispra, the Mark 11 and the Mark 13 cycles, is approaching to a conclusion.
The chemical reactions of these selected processes are the following:

Mark 11 $SO_2 + 2H_2O = H_2SO_4 + H_2$ (electrochemical step)
$H_2SO_4 = H_2O + SO_2 + 1/2\ O_2$

Mark 13 $SO_2 + Br_2 + H_2O = 2HBr + H_2SO_4$
$2HBr = Br_2 + H_2$ (electrochemical step)
$H_2SO_4 = H_2O + SO_2 + 1/2\ O_2$

At the level of the **laboratory scale,** the demonstration of the feasibility of the method was made with the operation of a complete circuit for the cycle Mark 13 since May 1978.
The analysis of the results of these experiments with the laboratory circuit, built in glass and quartz and working at atmospheric pressure, was concluded, after the continuous run for 100 hr. The data obtained with these experiments confirmed the good operation and showed that the design data and criteria were correct.
The second level for the demonstration circuits is the **technological scale.** Firstly, an effort was concentrated on the design of a demonstration loop, verifying the possibility of the use of available technologies and commercial materials, for all the sections of a complete plant. The design of the loop was also conceived for the verification of the H_2SO_4 decomposition under pressure and with metallic and ceramic material, on the basis of the new scheme CRISTINA, i.e. a flow sheet for the decomposition of sulfuric acid where the heat transfer is obtained by mixing the gas with hot air, instead of heating the gas throught heat exchangers. This new scheme simplifies the problems of construction materials, decreasing the investment costs for the plant.
The plant which was designed is composed of two main sections: a chemical section for the thermal concentration and decomposition of H_2SO_4, and an electrochemical section for the regeneration of H_2SO_4, and the hydrogen production. The chemical section, which is the essential part of the process and the high temperature step, was fully studied calculated and designed by JRC. For the electrochemical section, that is the synthesis of H_2SO_4 from SO_2, it was decided to consider the electrochemical oxidation corresponding to the Mark 11 cycle.
The nominal capacity of the facility is 10 Nm^3 H_2/hr, with a pressure of 25 bars, and a total electric input of about 100 kW.
The chemical engineering and mechanical design of all the equipment was completed verifying that with the new concept for H_2SO_4 decomposition it is possible the use of construction materials actually available for conventional technology.
Concerning the construction of the experimental facility, due to budget and time limitation it was decided to limit the construction of the demonstration loop to one component of the plant: the cracker of H_2SO_4, which is the high temperature section of the plant and one of the critical components in the scheme for the decomposition of H_2SO_4 using the hot air scheme.
The objective is (i) the demonstration of the feasibility of the improved scheme for the thermal decomposition of sulfuric acid, eliminating most of the metallic heat exchangers with the use of direct, hot air for the heat transfer, and (ii) the experimental definition of some important technological parameters useful for the design of an industrial pilot plant and for more accurate techno-economic assessment of the process.
The commissioning of the plant was successfully completed: chemical equipments were tested under pressure at room temperature, and heated up to about 700°C with hot air.
The results confirmed the design data concerning temperature profiles through the refractory materials and the performances of heat recuperator and superheater.
During the last tests, including also the introduction of SO_2 to verify the chemical conditions, unexpected difficulties arose with the lubrication system of the blower and the test programme had to be stopped.
It was however possible to have the first confirmation on the basis of the temperature profiles of the synthesis reactor as well as of the SO_3 decomposer, that these equipments work efficiently. A delay in testing is necessary, to replace the blower with a new one with modified lubrication system to eliminate the former inconvenients: the necessary time will probably be recuperated during the first months of 1984, for the conclusion of the planned, experimental programme.
The parallel activity on the study of the construction materials was concluded. After the long term tests which confirmed the good behaviour, in the corrosive conditions corresponding to the Cristina process, of Incoloy 800 and stainless steel AISI 310 at 900 °C and 700 °C respectively, some complementary tests were made to study the behaviour of high silicon alloys, specifically the RA330 and the Nicral C alloys.
Improved behaviours were found, and it is possible to point out an optimum content of Si in these alloys.
In the frame of the research on thermochemical processes it was already mentioned a possible fall out: a process for flue gas desulphurisation called Mark 13A because is based on the reactions of the Mark 13 process for thermochemical hydrogen production.
Techno-economic assessments and experimental verifications up to now performed and in progress have confirmed that this new process is rather promising and can be well competitive with the currently used processes for flue gas desulphurisation.
Further development is necessary, together with scale-up studies and experiments. JRC is collaborating with the service «Valorisation of new technologies» of the EC General Directorate XIII (Luxembourg) to perform further steps in the verification and development at industrial scale, in connection with commercial companies interested in the potential of the process.
In this framework a transportable bench-scale unit was built, to make tests with gas produced in the combustion of different fuels, particularly coal with various impurities contents.

A second subject which could be a fall-out of the research on thermochemical production of hydrogen is a study on the possibility to use the reaction of SO_3 decomposition and related experience accumulated for the thermochemical processes, for the problems of energy storage.
This shift reaction between sulphur dioxide and trioxide could be used to store solar or nuclear heat or electricity.

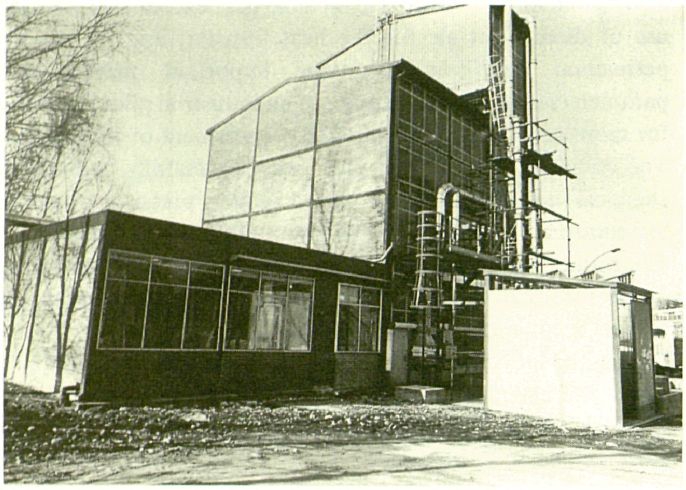

Fig. 3.

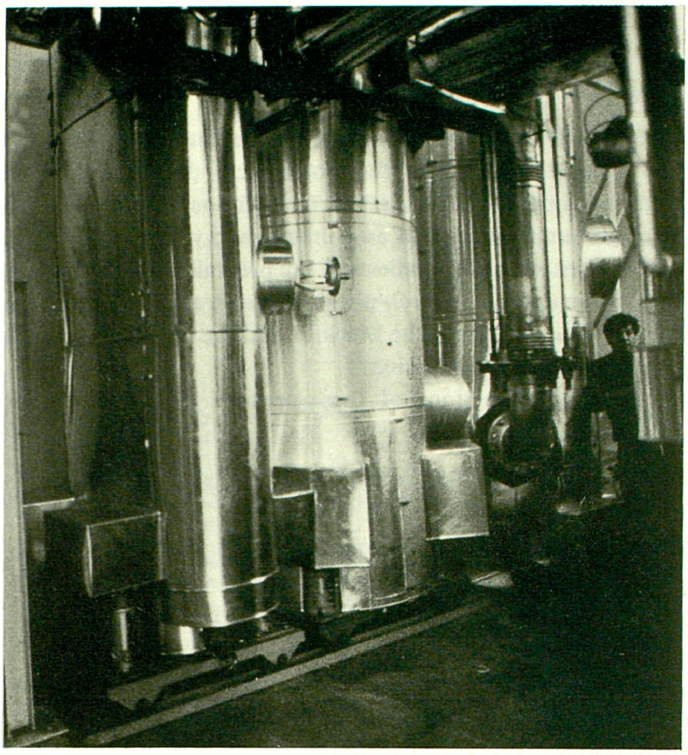

Fig. 4.

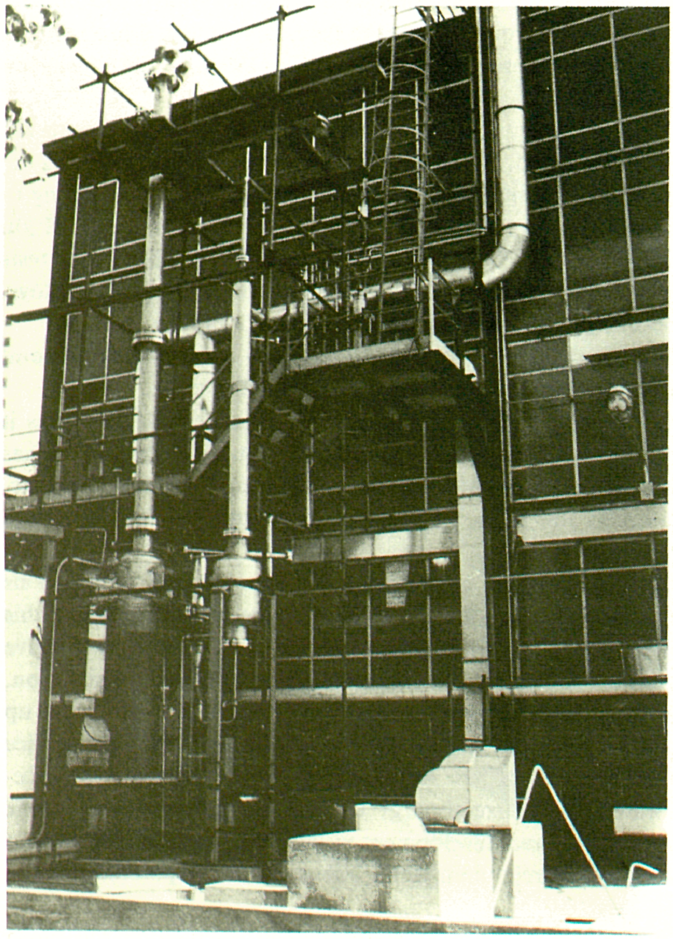

Fig. 5.

External views of the plant and some details

Fig. 6.

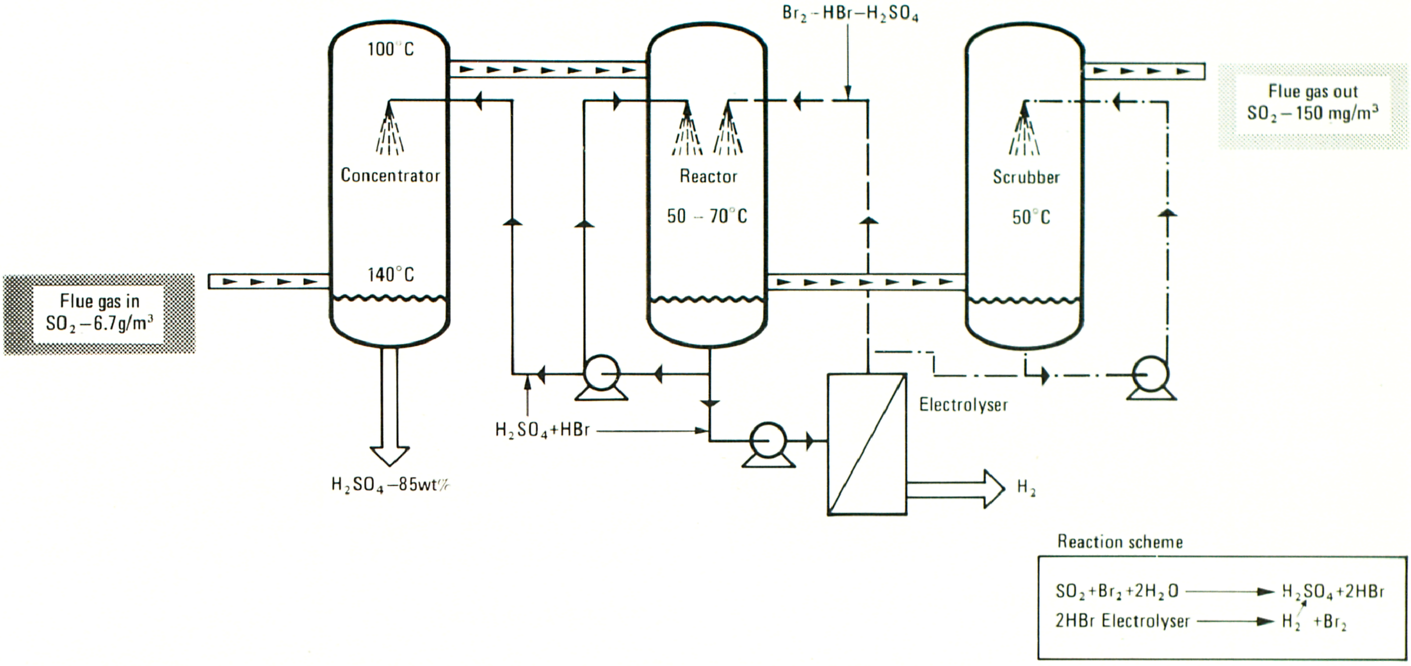

Fig. 7. The flue gas desulphurisation plant: block diagram

Storage consists of liquid sulphur dioxide and gaseous (40-60 bar) oxygen. Energy is delivered in electrical form, by regenerating sulphur trioxide.

Total storage volume required (at ambient temperature) is around 8 lt/kWh.

Corrosion problems are negligeables because no water is present inside the loop (SO_2, SO_3 and O_2 are the only employed chemicals).

No pollution problems can be envisaged because the system is entirely closed. Process technology is fully available.

Project II - Advanced Studies for Energy Carriers

The project is dealing with studies in different directions and in exploratory ways, in the field of energy transportation with some more attention to the problem of heat utilization; it started recently with a rather limited effort. The various orientations of the studies are here reported.

The activities on **Water Vapour Electrolysis** at high temperature continued, at low level of effort; studies were concentrated on some specific characteristics of electrodes behaviour.

Research on **Thermochemical Storage of Energy** at low temperature was oriented to some specific aspects, in connection with applications of solar energy at low temperature.

Main activities were on:

— measurements of heat storage capacity on two salts mixtures;

— corrosive tests for the evaluation of compatibility of phase change materials with containment materials.

Another activity in the field of utilization of heat is the research on **Heat Transformation**. Work is aiming to the demonstration of the feasibility of gas dynamic heat transformation. After theoretical calculations assuming laminar flows and turbulence, experimental studies were made and are in progress on cylindrical and conical condensers. A topical report summarizes the results.

Research in the field of storage and transport of heat is completed by the study of devices for **Passive Downward Heat Transport**. The activity is aiming to develop simple systems able to transfer heat downward without using electrical or mechanical energy for circulating the heat-carrier fluid.

These systems are particularly suitable for the low temperature applications of solar energy.

The technical unit previously described and able to transfer heat against an equivalent height of about 15 m was extensively tested. Results were well satisfactory in all the designed working conditions. In collaboration with the General Directorate XIII - Valorisation of new technologies (Luxembourg) a contract was signed with a specialized company for the construction and the design of a prototype, using a thermal collector (3 m^2) and able to transfer heat against an actual height of about 8 m.

The prototype was delivered and a complete system was assembled; construction, including instrumentation, was terminated and tests are starting.

The various activities of this project, **Advanced Studies for Energy Carriers**, are no more included in the 1984-87 Programme of the JRC, and therefore will be all discontinued. Only some experimental tests which are in progress, or ready to start, will be performed in the following months, in order to conclude the studies.

Project III. Study of Technical Systems

The activity progressed, at a limited level of effort, in the preparation and test of methodologies for energy and cost

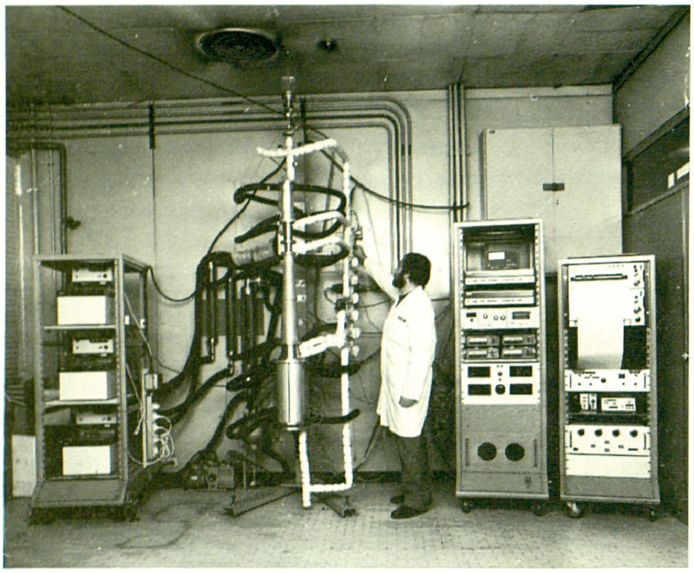

Fig. 8. Heat transformation: experimental set up for studying conical condenser performance

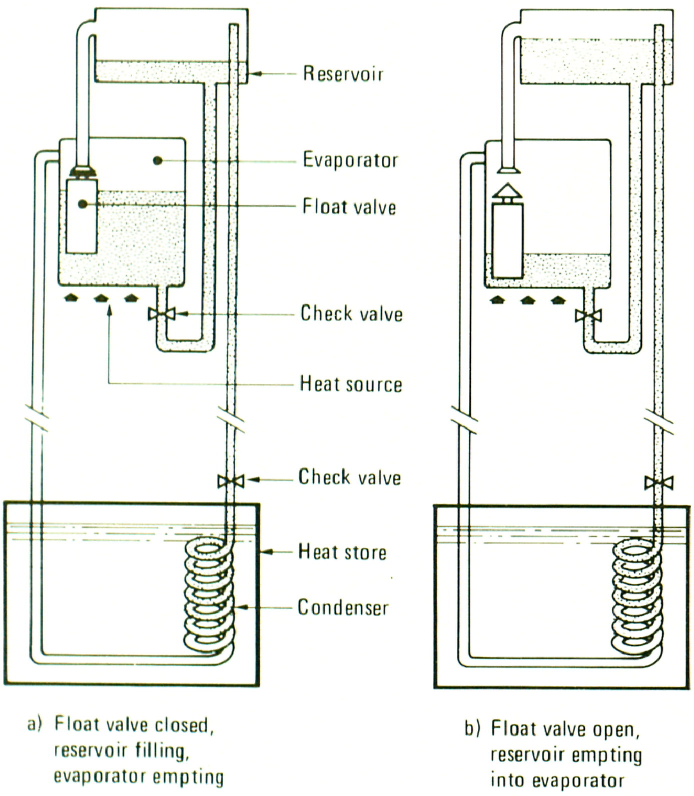

Fig. 9. Passive downward heat transport: diagram of the working principle

analysis, comparing different systems and different energy vectors.

The data base for the computer program for «Seaborne transportation of energy vectors» has been increased and improved. A paper on this program has been invited for presentation at the «Seatech Symposium on High Technology in Ports and Shipping», sponsored by C.E.C and held on 19-20 October, 1983.

Another subject is the analysis of some thermochemical systems for thermal energy storage and transport; the studies are made in collaboration with other research centres involved in the field.

In this framework, calculations are made concerning the use of thermochemical reversible reactions in the case of distric heating using low temperature heat from a coal fired power station. The aim is to verify the feasibility of such a type of thermal energy transport and storage system and to analyse, for a real and well defined case, the possible advantages in respect of a conventional hot water transmission system.

Studies are also made in view of possible applications of thermochemical energy storage and transportation in a practical case, as the reutilisation of industrial waste heat for industrial purposes, in a given area.

3. CONCLUSIONS

The evolution of the programme was done according to the general orientation of the pluriannual programme 1980-1983, i.e. terminating the research on thermochemical production of hydrogen and performing some exploratory studies in the field of energy vectors.

The project related to thermochemical hydrogen was oriented, in this last period, on the demonstration of the practical feasibility, with available technology, of the hydrogen production with thermochemical processes. Activities were concentrated on, and limited to, the construction and the testing of a technological circuit for the thermal decomposition of H_2SO_4. The circuit is limited to the cracker at 900°C and 25 bar of the mixture $SO_3 + H_2O$, but this is the critical, high temperature step of the thermochemical processes of the «sulphur family»; the scheme is using the process defined by Ispra, i.e. using mixing of hot air to transmit heat to the chemicals, having in this way the possibility to reduce the severe, corrosion conditions and to find commercial, constructive materials available today. The commissioning of the plant was successfully completed and the results confirmed the design data concerning thermal characteristics of the chemical reactors.

Delays in some deliveries and unexpected difficulties in the lubrication system made impossible to perform the planned test campaign; it is however possible according to the preliminary verifications confirm that the high temperature step of the thermochemical processes for hydrogen production, adopting the scheme patented by Ispra, is technologically feasible, today.

It has to be mentioned the good international connections existing and the leading role of JRC in the Task I «Thermochemical Processes» of the Agreement Hydrogen in the International Energy Agency cooperative programmes.

As a fall-out of this research a new process, for flue gas desulphurisation was patented, and tested, and there are good prospectives for applications.

Techno-economic assessments and experimental verifications up to now performed and in progress have confirmed that this new process is rather promising and can be well competitive

with the currently used processes for flue gas desulphurisation. JRC is collaborating with the service «Valorisation of new technologies» of the EC General Directorate XIII (Luxembourg) to perform further steps in the verification and development at industrial scale, in connection with commercial companies interested in the potential of the process.
For the project Advanced Studies on Energy Carriers, it can be said as a conclusion in the present phase that several preliminary studies were started, many with already some experimental results, as for chemical storage of heat, heat transformation and transport, high temperature water electrolysis, others only with orientative considerations (electrochemical storage, thermochemical processes for conversion of biomass into fuels, etc.).
The field of the various technologies for the storage, transport, utilization of heat at low temperature appears to be an important field in which the competences developed in thermochemistry can be usefully applied. Some promising techniques have been pointed out. However this research area will no more be included in the next 1984-87 multiannual programme; as a consequence the already limited effort on this project was decreased in this last year of the present 1980-83 programme, and no new activities were started.
For the same reason the activities on «Study of Technical Systems», the third project of the Programm, were slowed down due to the necessity to stop the work in 1984. Some studies were terminated, on seaborne transport of energy vectors, and preliminary analyses were performed on thermochemical transport of energy.
At the end of the four-year programme, it can be said that the research on thermochemical production of hydrogen reached its conclusion with the demonstration of feasibility of a process at pilot plant scale, and the orientative studies on new systems to transport energy, particularly heat, have put in evidence some research areas useful for an efficient energy management in energy systems.

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