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COMMISSION OF THE EUROPEAN COMMUNITIES

Multiannual Programme of the Joint Research Centre 1980-1983

1982 Annual Status Report

Hydrogen production, energy storage and transport

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HYDROGEN PRODUCTION ENERGY STORAGE AND TRANSPORT

1982

Research Staff: 40 men-year
Budget: 4.241.000 ECU

Projects:

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

Programme Manager: **G. BEGHI**
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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 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 present activities on hydrogen, which are going to a conclusion of the research phase, are progressively decreasing in favour of new activities on the more general aspects of energy storage and transport.
Research in the field of energy storage and transport is integrated into international efforts, when existing, and is of interest to all national and communitary bodies involved in the evaluation of the potential of future energy systems, and of possible new technologies.
The activities of the programme are subdivided in the three following projects:

- **Thermochemical production of hydrogen.**
  The experimental realizations, as a results of the previous programmes, will be terminated 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, on which to concentrate later on the effort.
- **Study of systems.**
  The aim is an evaluation of various, possible systems for collection-conversion-transmission-storage-utilization of energy under different conditions.

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.
All main equipments were delivered; many technical problems had to be solved, with useful information on the technological aspects. The installation is near full completion, including piping, electrical wiring and accessories. Commissioning will start in the first months of 1983, and the experiments with H_2SO_4 will be performed in the second half of 1983.
The scheme of the loop is given in Fig. 1. Some pictures of main equipments and of construction phase of the experimental facility are also reported.

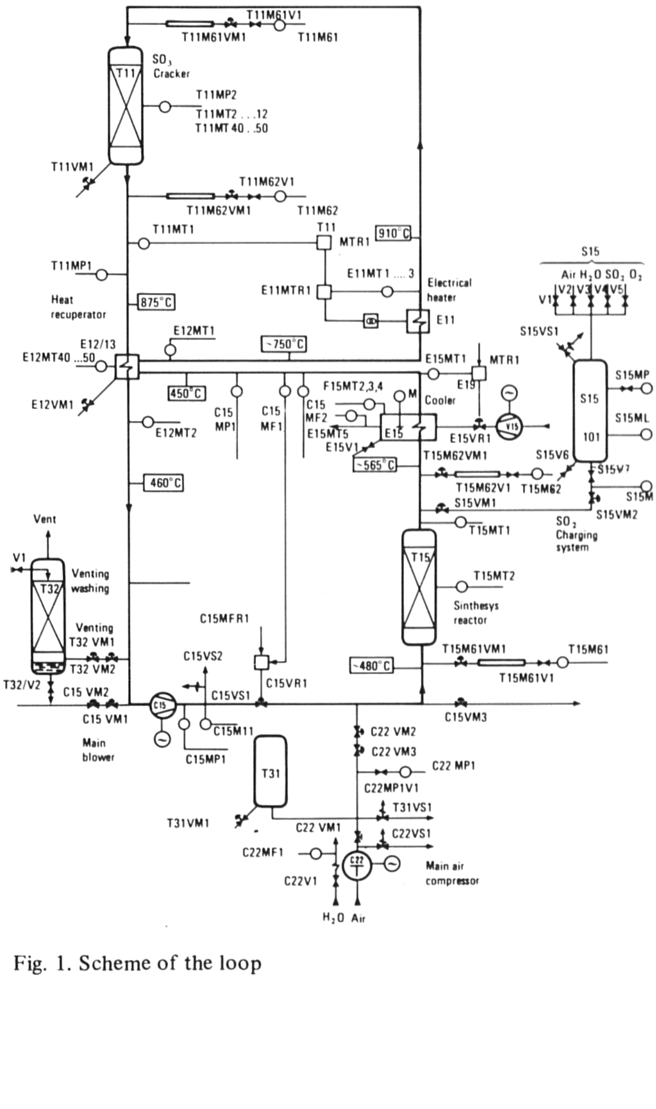


Fig. 1. Scheme of the loop

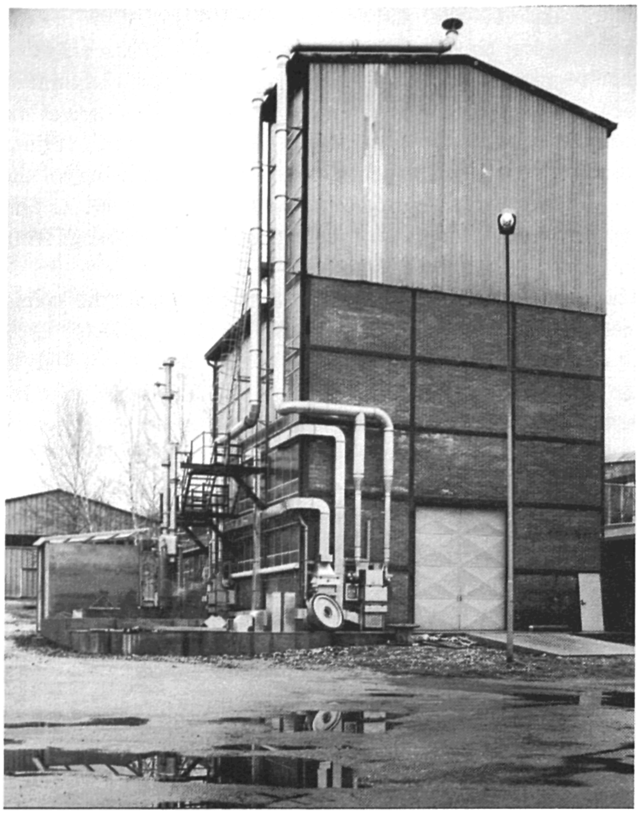


Fig. 2. General view of the CRISTINA experiment. On the left side of the building, the protection housing for the main air compressor C22 and the main venting system, can be seen. The height of the facility is more than 15 m

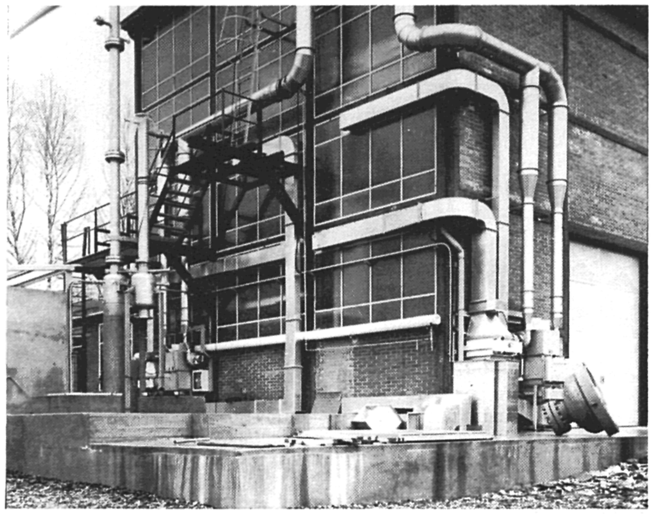


Fig. 4. On the left side Towers T31 and T32 for the process-air accomodation system can be seen, as well as the rear part of the compressor C22 housing. Main ducts are part of the normal and emergency venting system

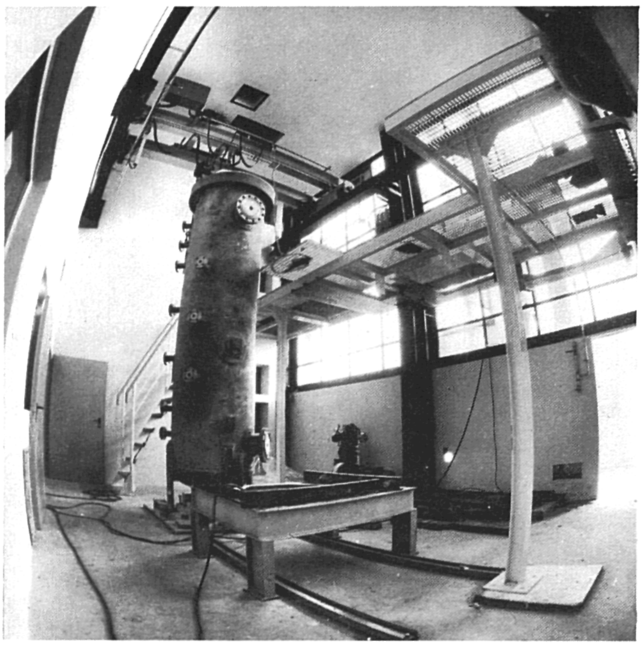


Fig. 3. A view of the high temperature zone of the CRISTINA experiment. The vertical apparatus is the sulphur trioxide cracker (decomposer) T11 in which sulphur dioxide and oxigen are formed. On the front, the place for the main heat recuperator E12/E13 can be seen

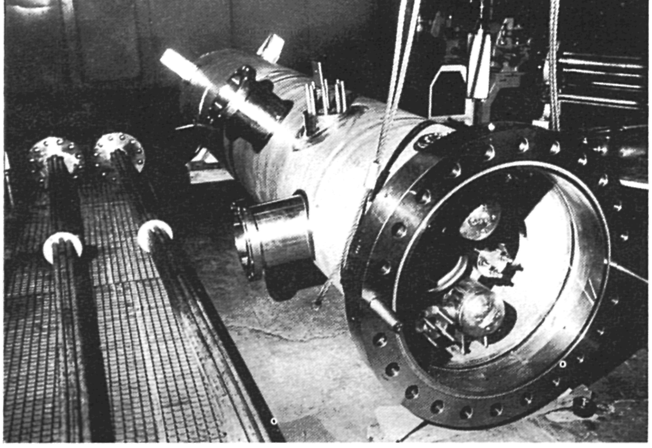


Fig. 5. A view of the open side of the main heat recuperator E12/E13. The heat exchanger heads are shown, as well the tubular group

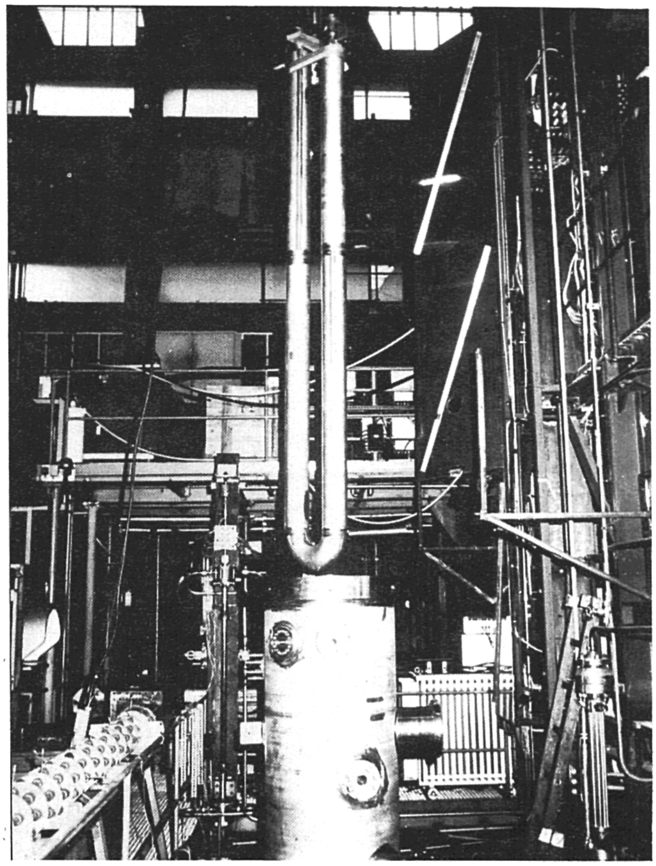


Fig. 6. A view of the main heat recuperator E12/E13, during the extraction of the tubular heat exchanger

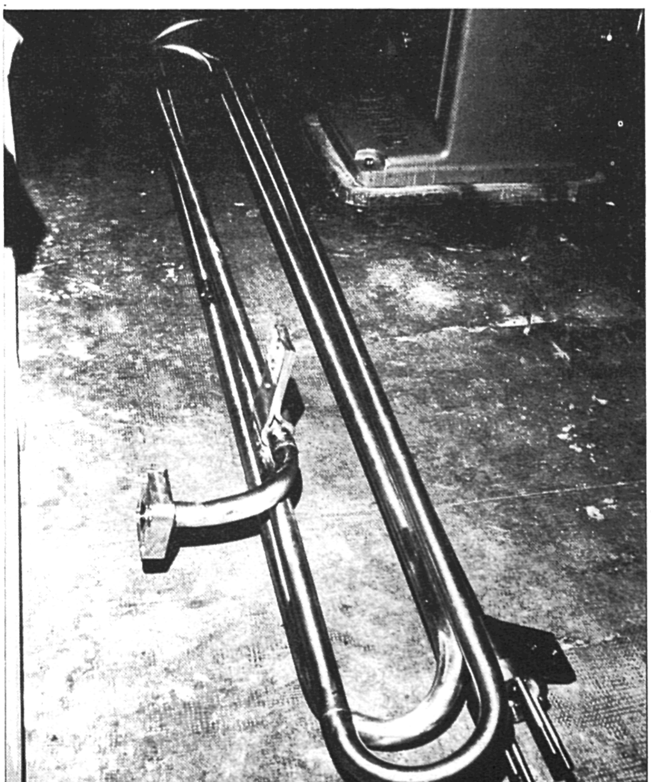


Fig. 7. A view of the electrical heater E11 in which the pneumatic and electrical connection are shown

In parallel to the activity on the construction of the technological circuit, activity on which most of the effort of the Programme is concentrated, particularly from the point of view of the budget, other activities are in progress such as the study of construction materials with corrosion tests. Previous results confirmed that Incoloy 800 is an alloy suitable for the use in the highest temperature section, up to 900°C and stainless steel AISI 310 for the temperatures in the range from 550°C to 700°C.

The corrosion remains within acceptable limits, the sound metal loss not exceeding 0.5-0.3 mm/year, respectively.

In view of possible improvements for the metallic materials in the range 700-900°C, tests were made with alloys similar to Incoloy 800 but with higher Silicon content: the positive influence of this element was put in evidence analyzing the behaviour of the already tested materials.

Two alloys were selected: Nicral C, produced by Creusot-Loire (France) with 1.92% Si, and RA330, produced by Rolled Alloys (USA) with 1.15% Si.

Tests made with temperature up to 900°C were concluded after 8500 hours (1 year).

Preliminary metallographic examination (see fig. 8) seems to show that the beneficial effect of Si content has a maximum, corresponding to an optimal concentration of this element near to 1 wt%. Accurate X-ray microanalysis should give details on the mechanisms of corrosion.

Some tests were made also on the preparation of coated alloys. Among the various techniques for the formation of protective coatings on various alloys, the plasma spray process is used. Ceramic deposits of magnesium zirconate and aluminium silicate on Inconel 600 were obtained.

Multilayers metallic undercoats were used to prevent fissuration of deposits. Tests are oriented now to reduce the porousness of the layers.

Other complementary activities in the field of thermochemical processes are those related to the electrochemical decomposition of HBr.

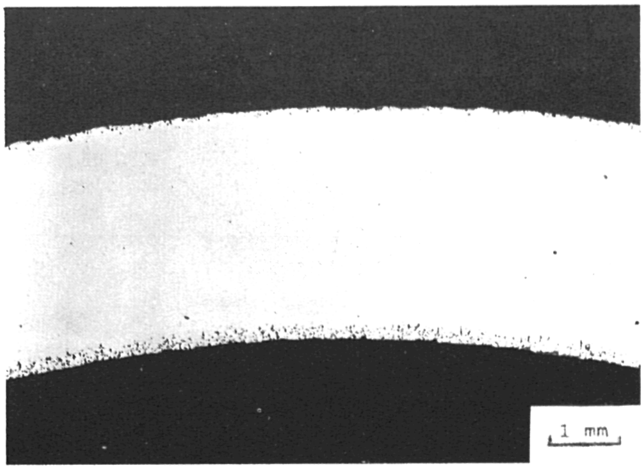


Fig. 8. Optical macrograph of a cross section of a sample taken from the 900 °C zone of the RA 330 tube after 8500 hours of corrosion

Preliminary measurements were made on cell working under pressure, up to 40 bars in order to have more compact and cheaper HBr electrolyzers. Application of pressure seems to give an effective improvement of cell performance.
In the frame of the research on thermochemical processes it was already mentioned a possible fall out: two of the chemical reactions of Mark 13 cycle (reaction of bromine with SO_2 and electrochemical decomposition of HBr) are well suitable as flue gas desulphurization process (patent pending).
This new process offers several advantages. It does not produce the huge amounts of valueless, disposable products, as are produced in the current throw-away processes, such as lime and limestone scrubbing.
The sulphuric acid produced is of high concentration and is directly produced in one single reaction step. No additional thermal regeneration step are required. The internal regeneration of bromine by HBr electrolysis produces a considerable stream of pure hydrogen, which is a very valuable by-product of the process. No solid materials or slurries are required as reactants.
Reactions rates are high and will probably only be diffusion controlled, so that reactors of relatively small dimensions can be utilized.
On the basis of a contract of the General Directorate XIII-Direction Technology Transfer (Luxembourg), with the Technische Universität Berlin a feasibility study of the process has been carried out by Prof. W Gestrich. The conclusions of this study are very favourable, with substantial reductions in the investment costs and running costs, rapported to the current processes.

During the reporting period, an experimental set-up was attached to a side stream of the flue gas from the power station of the Ispra Establishment; this power station is using a fuel oil with a sulphur content of about 2.5% w. A number of long duration runs have been carried out, showing that there are no major technical difficulties for the development of the process to an industrial scale. Other verifications are planned, particularly with flue gas from coal-fired power plants.

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. The project is in a phase of evolution, engaging at present a rather limited effort. The various orientations of the studies are here reported.
The activities on **Water Vapour Electrolysis** at high temperature are continuing, at low level of effort; studies are in progress on the behaviour of the cathodic interface between Strontium Doped Lanthanum Chromite (SDLC) and Yttria Stabilized Zirconia. It was found, as a «fall out» of the research, that SDLC may well replace Platinum as electrode material for oxigen partial pressure sensor at high temperature.
Research on **Thermochemical Storage and Transport of Energy** at low temperature was concentrated on a preliminary study on the ternary system NH_3-H_2O-LiBr as an example, and a candidate thermochemical system, able to work in the same conditions as the hot water systems used for district heating. A specific flow-sheet was defined and calculations were made of mass and energy balances.
These data are used for economic evaluations and comparisons.
Always in the field of chemical storage attention was maintained on the two reciprocal salt pair systems already selected: Barium-Potassium and Barium-Sodium-Nitrates in view of the verification of possible applications. In collaboration with DFVLR (Stuttgart) these salts will be tested in a technological unit for latent heat storage.
Theoretical considerations were also started on the concept of **«chemical heat pump»**, able to upgrade, partially, heat available at low temperature, through reversible chemical reactions. An example of application could be the possibility of upgrading industrial waste heat of about 50-60°C in combination of storage of this energy. Preliminary measurements are in preparation.
Research in the field of storage and transport of heat is completed by the study of devices for **Passive Downward Heat**

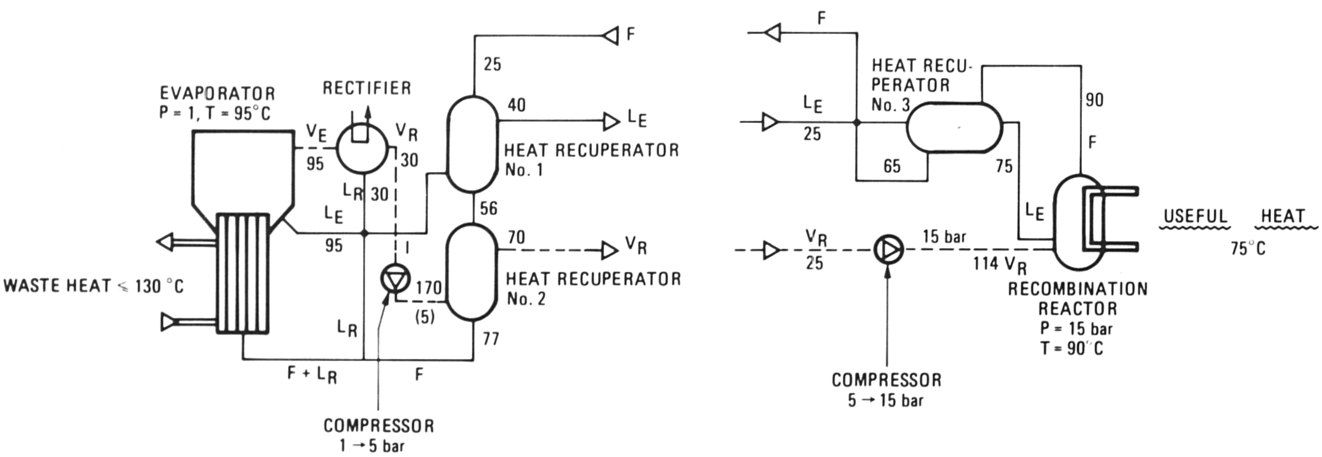


Fig. 9. Thermochemical energy transport system based on $NH_3/H_2O/LiBr$

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.
After the first models builts and tested in the previous periods a new system was patented, working without pressurizing gas.
A version of this new system was built during the reporting period and thoroughly tested, giving results in full agreement with the design conditions.
After the test of a laboratory model, during the reporting period a technical unit was assembled and tested, working under pressure, up to 15 bars, and using Freon 114 as working fluid. It is possible to heat a heat store medium located at up to 15 m down. The technical unit worked quite well in all the tested conditions. In the meantime, through the Directorate Generale XIII-Direction Technology Transfer (Luxembourg) a contract is being signed with a small industrial company for the design and the construction of a first industrial prototype, already integrated with a solar heat collector working with a boiling fluid.
In view of the orientation of future work in the field of heat utilisation, storage and transport, an international Workshop on Chemical Storage of Thermal Energy was organized at Ispra, on 15-17 December 1982, with the participation of about 20 experts coming from European Laboratories active in the field.

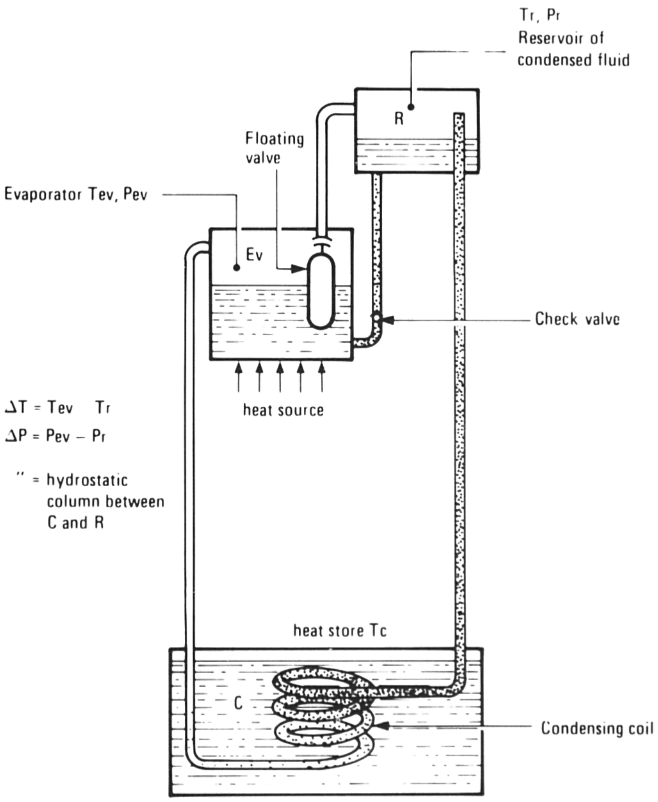
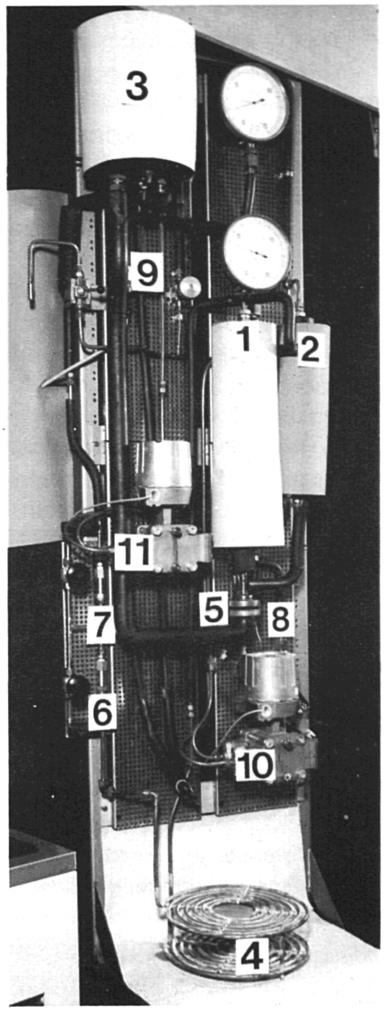


Fig. 10. Scheme of working principle



1. Boiler
2. Floating valve
3. Reservoir
4. Condenser
5. Check-valve
6. Pressure reducing valve
7. Pressure reducing valve
8. Pressure transducer
9. Pressure transducer
10. Level transmitter
11. Level transmitter

Fig. 11. The technical unit

Project 3. Study of Technical Systems

The activities are concerning techno-economic assessments of technical systems for storage and transport of energy, and are progressing at a limited level of effort.
Various technical systems of conversion, storage and transport/transmission of energy, using different «energy vectors», are studied and compared to evaluate their relative merits using two criteria. These criteria, which are based on delivery of one unit of usable energy at a given point of the economic systems are:

— cost, in «constant money» (i.e. $/GJ)
and
— energy requirement (i.e. GJ/GJ).

The activity is progressing, at a limited level of effort, with the following objectives:

(i) definition of different technical energy systems.
(ii) preparation and test of methodologies for energy and cost analysis.
(iii) comparison of different systems.

The technical systems taken into consideration include:

— as primary energy: natural gas, coal, solar, nuclear

— as energy vectors: natural gas, coal, hydrogen, methanol (ammonia)

The step «transport» of the energy (raw materials and energy vectors) is studied for all the possible forms (on-shore and off-shore pipelines for liquids, gases and slurries, ships if liquid, solid or slurry, train, barges, etc.).

The complete results would be:

— the energy requirements calculated for each technical system considered;

— the comparison of technical systems; the relative merits of the systems for conventional and alternative energy vectors are put in evidence and quantified;

— identification of the steps of the technical systems, requiring technological improvement and for which energy savings are possible;

— the recovery time of the invested energy for each technical system considered.

Concerning the computer codes, the preparation of the computer program for «pipelines transmission of fuels,» (first part-gases, on-shore and off-shore transmission) has been completed. Work on liquids and slurries transmission is in development.

The computer program for «seaborne transportation of fuels» has been also completed after improvement; the data base is under completion. 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., which will be held on 19-20 October, 1983.

These two computer programs will be an important help for the study of the energy transmission/transportation step of the energy technical systems.

A collaboration with specialized organizations has been undertaken for slurries seaborne transportation. The resulting study will be presented in March/April 1983 at the eighth «International Conference on Slurry Transportation».

An exploratory study on the utilisation of low temperature in dustrial waste heat by thermochemical transmission and storage for the district heating sector, has been carried out; some preliminary results have been obtained. These evaluation will be particularly useful in defining the conditions for which thermochemical systems can be competitive and in selecting the chemical reactions more promising and requiring additional experimental research.

3. CONCLUSIONS

The evolution of the programme is following the orientation given for the multiannual 1980-83 programme, i.e. the shifting of the main effort of research from thermochemical production of hydrogen to other «energy carriers» in the general field of storage and transportation of energy. These studies could give useful contributions to the technologies related to energy storage and transport, which are becoming more and more important for the valorization of new, renewable energies, and also for some aspects of energy conservation.

The first project, Thermochemical Production of Hydrogen from water, is concentrated now on 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. Most effort of this project is now concentrated on this demonstration loop, which will be the final step in the JRC research phase, concluding the studies started 10 years ago.

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: industrial companies have already shown an interest in the development.

For the second project, Advanced Studies on Energy Carriers, it can be said as a conclusion in the present phase that several preliminary studies are in progress, 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.).

These studies are preparing the background for decisions to be taken for the future programme. The field of the various technologies for the storage, transport, utilization of heat at low temperature seems to be prioritary.

The third project, Study of Technical Systems, will give a contribution, limited due to the low level of effort but well specific, to selections and decisions concerning different systems for solving the problems of converting and transporting energy, in large quantities and over long distance, and of storing thermal energy.

The elements prepared for the selections are based both on economic and energy analysis, useful not only for decisions convenient in the short time but also in a more general, long term view. An evaluation of the emissions in the environment, from the different systems, will give another parameter useful for the comparison of the systems also from the point of view of pollution.

As a general conclusion, we can say that, following the decisions of the JRC Pluriannual Programm, this Programme is fully in the transition phase, being near to the conclusion the activities on Thermochemical Hydrogen and starting research in the new orientations of the larger objective of energy storage and transport.

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