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COMMISSION OF THE EUROPEAN COMMUNITIES

Multiannual Programme of the Joint Research Centre 1980 - 1983

1980 Annual Status Report

Hydrogen production, energy storage and transport

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HYDROGEN PRODUCTION ENERGY STORAGE AND TRANSPORT

1980

Research Staff: 40
Budget: 3,826,000 ECU

Projects:
1. Thermochemical Production of Hydrogen
2. Advanced Studies for Energy
3. Study of 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 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 will still be important at the beginning of the programme are going to a conclusion of the research phase, and will progressively decrease in favour of new activities on the more general aspects of energy storage and transport, which will become the essential part of the programme at the end of the four-year period.

The activities of the programme are subdivided in three projects, each one having a different evolution of their importance in the time.

The first project is the **thermochemical production of hydrogen:**
in the first two years of the programme the experimental realizations prepared in the previous programme will be terminated. The objective is to verify the technological feasibility and the competitivity of the thermochemical hydrogen production route on a industrial scale; a final report describing a pilot plant will be produced. Consequently, during the third year of the programme, the technical and economic studies on thermochemical hydrogen production will be terminated.

The second project deals with **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 and basic nature is useful for defining and evaluating various ways to transport and store energy. The project starts with definition and selection of various techniques, on which to concentrate later the effort.

The third project is **study of systems:** evaluation of various, possible systems for collection-conversion-transmission-storage-utilization of energy under different conditions. Comparison of available date, techno-economic assessments, collection of experimental data, safety assessment.
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.

2. RESULTS

Thermochemical Production of Hydrogen

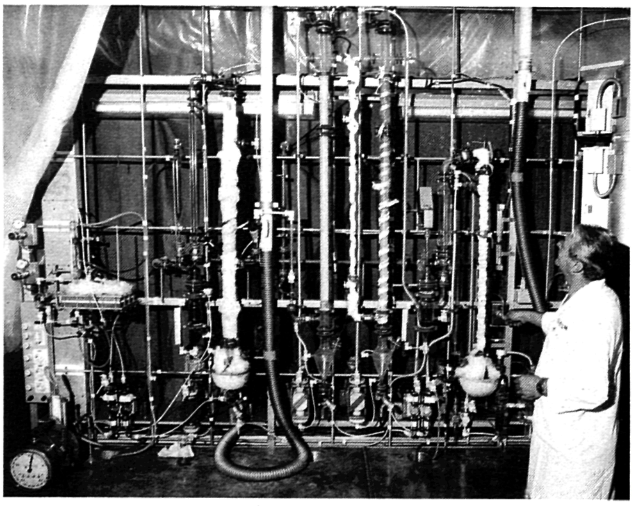
The objective of the activity is the verification of the feasibility and the competitivity of the thermochemical decomposition of water, as a possible new method for hydrogen production, using high temperature heat as primary energy.

After the exploratory studies and the preliminary tests made in the past years, the research phase is approaching to a conclusion with the demonstration of the feasibility of two of the cycles defined at Ispra, the Mark 11 and the Mark 13 cycles. This demonstration is made at two levels: laboratory scale and technological scale.

Complete circuits

At the level of the **laboratory scale** a complete circuit for the Mark 13 cycle was put into operation in May 1978, with the following objectives:

- verification that the conversions and the concentrations of the chemical reactants can be reached and maintained
- to check the possible formation of unexpected by-products
- to investigate process control problems connected with the continuous operation of a closed cycle process.



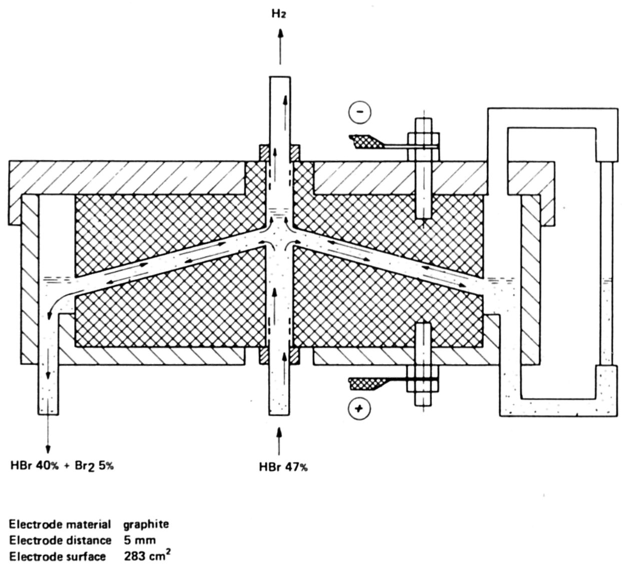
Laboratory-circuit for MARK-13 cycle

The experiments performed with this laboratory scale circuit, (nominal capacity of 100 lt H_2/h) and particularly the long duration continuous runs (about 100 hours each), provided the demonstration and confirmation of the above mentioned objectives. The working programme for the circuit was therefore considered successfully concluded: all the information possibly coming from this demonstration laboratory plant was obtained, and was confirming the previous positive results, and that the design data and procedures were correct.

In addition to the result coming from the operation of the complete, closed cycle, other particular and interesting results were obtained during the last experiences.

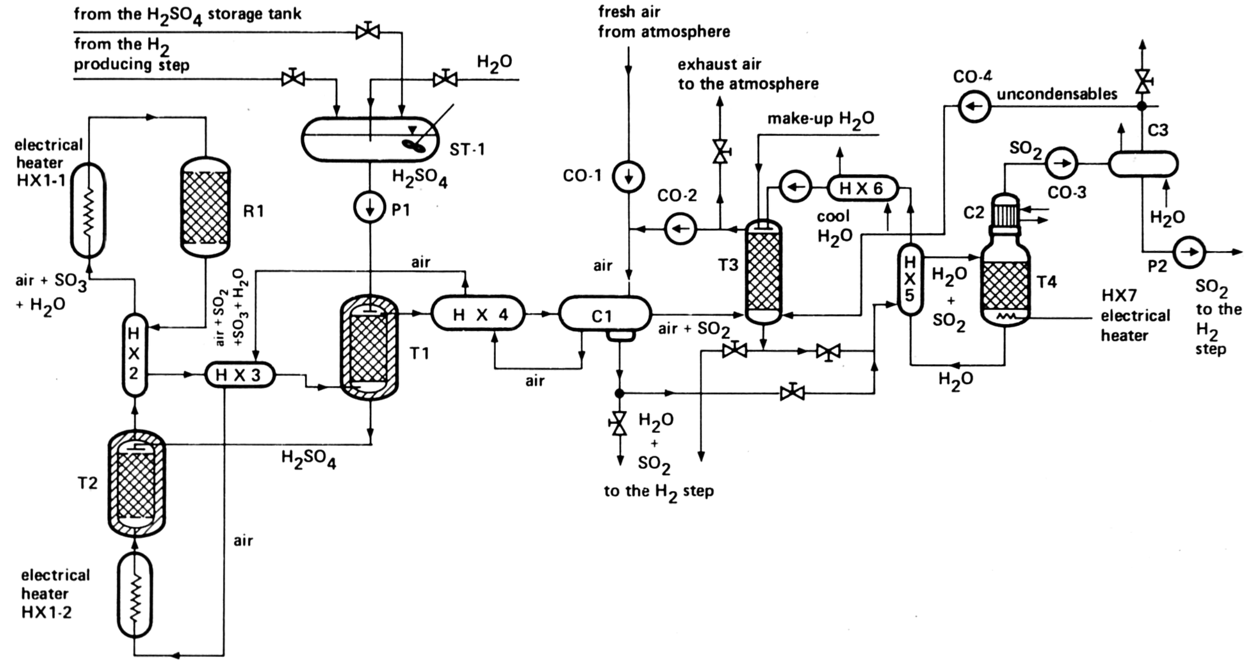
Concerning the high temperature step, i.e. the thermal decomposition of SO_3 at temperatures in the order of 1150 K (about 850 °C), it was found, and confirmed, that the up-to-now used catalyst for this decomposition can be avoided, and the catalytic effect of metallic (stainless steel or Incoloy 800) packing materials is sufficient for the reaction of decomposition. The solution for the SO_3 decomposer reactor replacing the expensive catalyst with a common, cheap, metallic packing materials is attractive and seems well feasible.

Concerning the electrochemical step, the decomposition of HBr, various designs of the electrochemical cell were tested, and some improvements were obtained, for the main parameters and for the stability of the behaviour. Current densities above 300 mA/cm² were not possible.



Circular electrolytic cell counter current

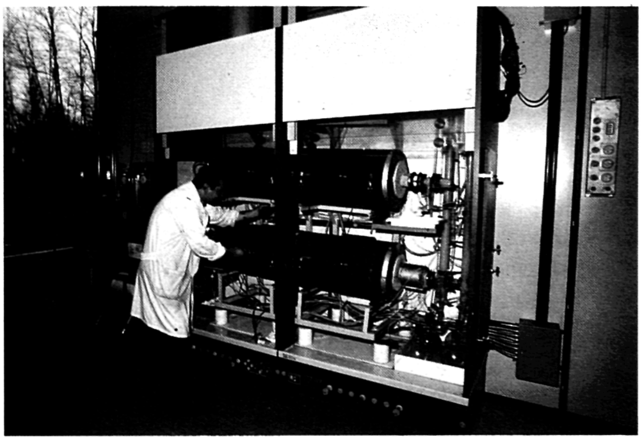
The second level for the demonstration circuits is the **technological scale.** A technological circuit is in preparation, for the verification of the H_2SO_4 decomposition under pressure and with metallic and ceramic material, on the basis of the new scheme CRISTINA, i.e. a flow sheet for the decomposition of sulfuric acid when the heat transport is obtained by mixing the gas with hot air, instead of heating the gas through heat exchangers. This new scheme simplifies the problems of construction materials, decreasing the investment



Project chris semplified scheme

costs for the plant. Another objective will be the chemical engineering analysis of the different chemical reactors, in order to obtain main elements for designing larger units.

During the year 1980 there was a delay of some months, in the planned schedule for the preparation of this technological circuit, due to (i) some financial difficulties at the beginning of 1980, (ii) results of experimental measurements on vapour-liquid equilibria in the system H_2SO_4-H_2O giving data slightly different from the original assumed data for flow-sheet calculations and obliging to redesign some apparatuses.
The design of all equipments and accessories of the circuit has been completed and most of the components (chemical apparatuses, instrumentation and control, data processing system) are on order.



Facility for corrosion test

Materials

Corrosion tests are made in order to have information useful for the construction of the technological circuit, and also for the evaluation of investment cost of large industrial plants in the frame of the techno-economic assessments.

After the screening tests made during the last years, and the selection of promising candidate materials, always using commercially available alloys, work was concentrated on corrosion test for the more critical section of the flow-sheet: the sulfuric acid decomposition. Important tests have been made during 1980: tests of long duration (up to 1 year) and made on tubes, instead of the small specimens.

The tubes under test are of Incoloy 800 and stainless steel AISI 310, the corrosive environment is constituted by the decomposing sulphuric acid with added air. The temperature ranges are respectively 1000 ÷ 1200 K, and 670 ÷ 1000 K; as it was foreseen in the planned activities, the tests have reached the duration of 8500 hrs (1 year of operation) and about 5000 hrs, showing an acceptable small degree of penetration of the attack.

Analysis and measurements have been started on the Incoloy 800 tube, tested 1 year, for a detailed study of the results, that are in any case already encouraging.

In view of possible improvements of the performances of the commercial alloys, studies are in progress also on protective coatings. The coatings more effective against that corrosive environment are those cointaining Al or Cr or Si, whose oxides are higly protective. In some cases, to prevent depletion of the active element, due to solid diffusion at high temperature in the base alloy, a diffusion barrier is also necessary. The study under way is to identify the suitable coatings and diffusion barriers (TiC, TiB_2, $MoSi_2$, etc.) and the operating conditions for their deposition by the plasma spray technique.

Optical micrography of cross section of Incoloy 800 sample corroded for 8500 hours at 1200 K (100 X)

Electrochemical Cell for HBr

Another complementary activity to the technological circuit concerns the electrochemical decomposition of HBr.
The cathodic discharge of hydrogen in hydrobromic acid solutions has been studied on palladium electrodes, and on graphite electrodes activated by the electrodeposition of palladium. Palladium, although not stable in the acid solution when not cathodically protected, is able to reduce the cathodic overvoltage to the low values obtained with platinum as electrocatalyst; however, the amount of palladium necessary for reaching this results is about ten times higher than that of platinum.
Tests are also conducted on a complete cell, with vertical bipolar, graphite electrodes and with a suitable diaphragm to keep separated the anolyte from the catholyte. On this cell measurements of the influence of various parameters (temperature, electrolyte composition etc.) have been started.

Advanced Studies for Energy Carriers

The first year of the multiannual 1980-83 programme is also the first year for this project which is an extension of the research from thermochemical hydrogen to other subjects in the field of storage and transportation of energy.

Activities concerning this project are starting and are in a preliminary phase of definition and selection, on the basis of previous experience already existing at the JRC and of the needs of research in the field.
Several potentially attractive subjects, suitable to give contributions for storage and transport of energy, have been considered. In this preliminary phase of the project only on some of them experimental activities were performed; some results were already obtained.

Hydrogen production from water is considered, from the point of view of the heat source: studies are in progress to evaluate the possibility and the limits of the solar heat furnaces for these applications and to check whether there exist cycles that are better coupled with the isothermal high temperature heat available by this way than with the non-isothermal heat from the High Temperature Reactor.

A limited activity is also started on advanced methods for water electrolysis, with the usual goal of reducing the necessary amount of electrical energy. In this frame, tests are in progress on the high temperature steam electrolysis using zirconium oxide as electrolyte. The research is centred on the behaviour of cathodic electrocatalyst, and on the stability of the electrolyte at the cathodic side. This kind of electrolysis finds its natural place where there is available, together with the electrical energy, also heat at high temperature.

The orientation of this research is well complementary to the programme of the Indirect Action.

Another activity, in the field of thermal energy storage, is the study of chemical latent heat storage systems. In these systems an endothermic reaction is used to load the store and the reversed exothermic reaction is used to restitute the stored energy when needed.

During the reporting period, experimental tests were continued on the previously studied systems using barium salthydrate and two reciprocal salt pairs, sodium and potassium nitrates/hydroxides. Cycling tests are performed to determine the most favourable temperature intervals: 70 heating and cooling cycles are normality, using small volumes of about 10 cm^3 in the temperature range of 30 - 90 °C. One of the systems showed no deterioration of heat storage capacity after these cycles, the heat storage capacity of the second on the contrary decreased during the cycling test but returned to the initial value after an interruption for about 60 hours, indicating small crystallization rates. In parallel to these laboratory scale experiments, a technological experiment was prepared for testing a latent heat storage system of technical size (about 1 m^3). The system, consisting of small plastic spheres filled with the heat storage medium in an upward water flow, will be tested in the frame of the Solar Energy Programme.

Besides this, the possibility of a collaboration with DFVLR Stuttgart for the construction and operation of another latent heat storage system has been examined.
A modification of an existing system and its operation with the two reciprocal salt pair developed at Ispra are foreseen.

Another subject of research is the verification of the possibility of realization of a "heat transformer", i.e. a device for changing the temperature of heat in a nearly reversible way without receiving any other input that heat and without delivering anything else than heat. The basis is an idea already developed at Ispra, which makes use of gasdynamic effects and evaporation and condensation at the container walls.

During the reporting period, an improvement was made to the computer code, previously developed, for the optimization of the vapour duct of the heat transformer. The preparation of an experimental set-up for testing the concept was also started.

The activities of this project are in a preliminary phase, and priorities will be defined according to the evolution of the research.

Study of Systems

The activities concerning this project are in a first phase, and are limited to techno-economic assessments of technical systems for storage and transport of energy. The studies are based on previous experience made in the last years for some specific evaluations and assessment.

Various technical systems of production, conversion, storage and transport/transmission of energy in the form of various "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, using the device of "constant money" (i.e. \$/GJ) and

— energy requirement (i.e. GJ/GJ).

Information is identified and assembled on the appropriate energy vectors as a function of foreseeable energy sources and means of processing and transformation, storage and transportation/transmission within a system where easily accessible oil and gas become depleted or economically unattractive: this is done both for renewable and non-renewable energy source.

Elements are considered to optimize each technical system with regard to various criteria taking into account spatial (geographical), technical and resource factors.

The main results are:

— 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;

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

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

The technical systems taken into consideration include:

— as primary energies: natural gas, coal
hydrogen, 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, trains, barges, etc.).

The technical systems for which definition of details and collection of specific data are in progress, are at present the following:

— **natural gas:** production, on-shore and off-shore pipelines transmission; production, liquefaction, storage, seaborne transportation, regasification;

— **coal:** production, preparation, slurry pipeline transmission, transportation by train, dewatering, drying;

— **hydrogen:** production by electrolysis, storage, pipeline transmission, liquefaction, seaborne transportation, production of electricity by hydroelectric plants, nuclear plants and solar plants (thermal and photovoltaic);

methanol: a) production from natural gas and from coal (conventional processes), storage, pipeline transmission, seaborne transportation; natural gas supply by pipeline, coal supply by slurry pipeline and by trains;

— **methanol:** b) production from coal and non-fossil derived hydrogen, storage pipeline transmission, seaborne transportation.

For each specific technology, where possible, the calculation will be made using computer programs. A computer program has been prepared both for cost and energy requirements calculation for natural gas and hydrogen transmission by on-shore pipelines. A computer program for off-shore pipelines is in preparation.

Another computer program has been prepared for calculating the composition of the fleets necessary to transport, on routes of different length, given annual quantities of various energy vectors (oil, coal, methanol, ammonia, liquefied natural gas, liquefied hydrogen, etc.).

For cost analysis, the conventional methodology is used; the data are collected, as far as possible, directly by European and extra-European industries and organizations.

Energy requirements are calculated using the energy analysis method.

During 1980 work progressed with studies on technical systems of production, storage and transportation of methanol produced by natural gas, coal (conventional process), coal and non-fossil derived hydrogen. Two technical systems for coal (transportation by trains and transmission by slurry pipelines) have also been considered.

Some results of these comparisons, both from economic and energetic point of view, will be presented at scientific conferences.

In the frame of the study of technical systems another subject of study is an engineering analysis of specific thermochemical energy storage systems. A collection of information is in progress on all known thermochemical systems using reversible chemical reactions. Some systems will be selected, analysed with a computer code, and the technological flow-sheets will be defined. The results could be useful as an aid for orientating possible experimental work.

3. CONCLUSIONS

In this first year of the new multiannual 1980-83 programme we had the beginning of important modifications in the programme, shifting the main effort from the research concentrated on only the thermochemical production of hydrogen to an extension to also other items, other "energy carriers" in the 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, on thermochemical production of Hydrogen from water, is almost completely oriented now to the construction and operation of a demonstration circuit representing the conclusion of the research phase.
The work performed at Ispra is a large part of the european research in this field and could give an answer for the evaluation of the potential of this possible new method for hydrogen production. In fact almost all activities on this item in the EC are connected and oriented to the JRC final experiment, particularly the researches which are performed in the Energy R and D Programme-Indirect Action (Hydrogen, Project A of the Directorate General for Research and Science).

The second project is in a first, preliminary period and exploratory researches, based on competences previously developed at the JRC, would bring new ideas on some advanced studies concerning the energy storage and transportation. Some main orientations are in phase of definition and are generally in connection with similar activities in progress in various laboratories.

The third project, also on the basis of existing competences and still in a preliminary period, could give a contribution to selections and decisions concerning different systems for solving the problem of converting and transporting energy, in large quantities and over long distances.
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.

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