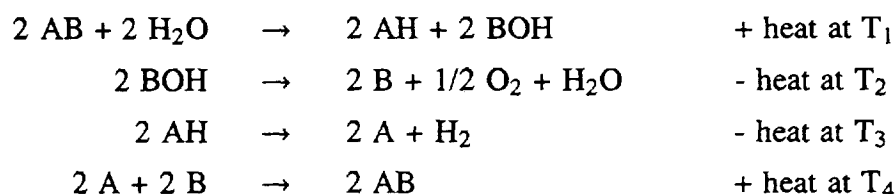


Appendix A

THERMOCHEMICAL CYCLES FOR HYDROGEN PRODUCTION

A.1. PRINCIPLE

Since a direct thermolysis of water, which requires temperatures of $> 2500\text{ }^{\circ}\text{C}$, is not practicable under normal circumstances, the splitting process is subdivided into different partial reactions, either one running on a lower temperature level. The principle is given by the following cycle:



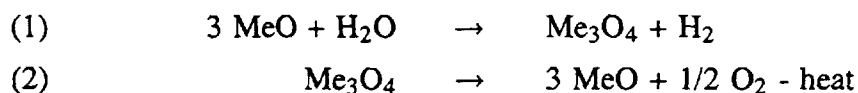
After the first cycle (vanadium - chlorine) was proposed in 1964, some 2000 - 3000 potential thermochemical cycles have been tested and checked in terms of appropriate reaction temperatures and velocities and in economic respect. Thermochemical cycles are Carnot cycle-limited meaning that high temperatures could improve the conversion efficiency. Major problems arise by the large material flows, by the introduction of impurities, and by the potential creation of toxic and environmentally unacceptable species. The main goal is to achieve satisfactory overall energy efficiencies which are currently not higher than around 40 % and, in connection with separation steps and severe materials and equipment design difficulties, do not allow, so far, large-scale thermochemical process applications [11]. Studies are focusing on reaction kinetics, thermodynamics, reactant separation, material stability, flow sheeting, and cost analysis.

Thermochemical multistage cycles are usually classified in families according to the chemicals involved. Cycles can consist of up to 8 equations, usually 3 - 6, with up to 5 elements others than H_2 and O_2 involved [5].

A.2. THERMOCHEMICAL CYCLES

A.2.1. Oxide System

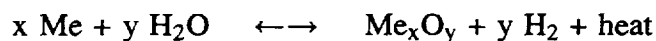
The most simple water splitting process is the two-step cycle with metal oxides (MeO) as the redox system



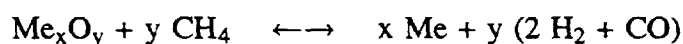
where Me = Mn, Fe, Co

The High-Temperature Solar Chemistry Section of the PSI in Switzerland has realized a sunlight-concentrating device based on the metal iron (Me=Fe) with a power of 60 kW to provide the required temperatures of 2200 °C (for step (2)). Efficiency is expected to be 20 % [13].

In other cases of water splitting reactions, the metal reacts exothermally with water at a temperature < 800 K [13]



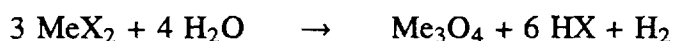
For the electrothermal dissociation of metal oxides into their elements, high temperatures are needed which can be lowered by using chemical reducing agents. The combination with CH₄ as a reducing agent in a reforming process results in the coproduction of metals and synthesis gas:



Due to its molar ratio, the synthesis gas mixture is particularly suitable for methanol production. The iron system, Me = Fe, has been extensively studied in laboratory electric furnaces [13]. The other two systems have a very low hydrogen yield only [9].

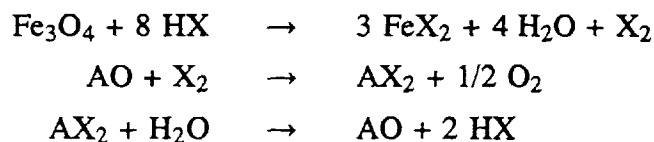
A.2.2. Halide Family Processes

In the **metal-halide system**, the hydrogen producing reaction is written as [9]



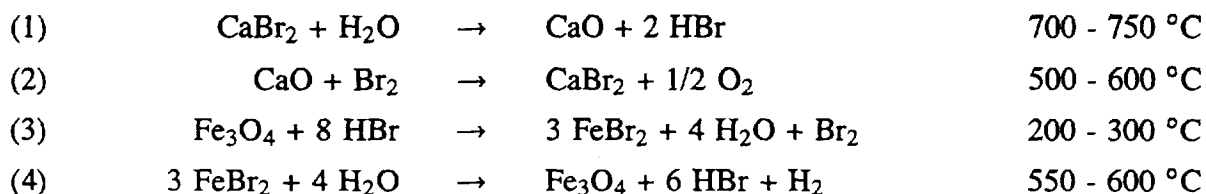
where Me = Mn, Fe
X = Cl, Br, I

The Mn system is insignificant due to negligible yield of hydrogen. For the oxygen producing reaction, three main reaction paths have been proposed. In one of them, the oxidizing reaction of H₂O is conducted in two steps through the addition of an oxide phase which reacts to give the corresponding halide [9]:



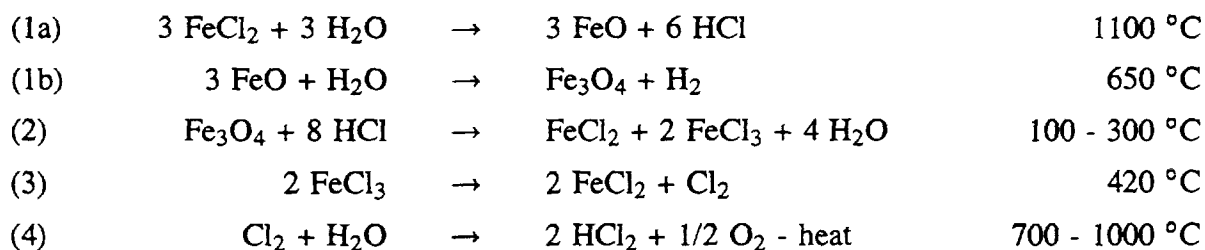
where A = Mn, Ca
X = Cl, Br

The **bromine-calcium-iron process** based on the combination A = Ca and X = Br is also named “UT-3” (University of Tokyo-3) process:

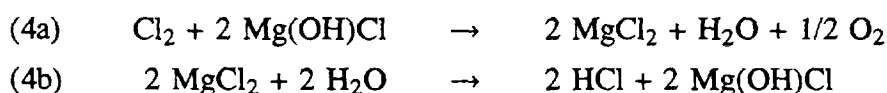


Stages (1) and (3) produce reactants for the stages (2) and (4). All reactions in the UT-3 cycle are solid-gas reactions with the net result of a steam decomposition into H_2 and O_2 [16]. Therefore it is easy to separate gas from solid products. The process has four reactors connected in series in a loop. After one cycle, the reactors are switched and the direction of the cycle is reversed. Solid reactants are given in the form of spherical pellets. Heat exchangers are used to regulate reaction temperatures. Conversion rates for some reactions are small meaning that gas flow and thus reactor size is relatively large.

Another promising thermochemical cycle is based on the “**iron-chlorine compound**” (or “Mark 9”) [4, 8]:

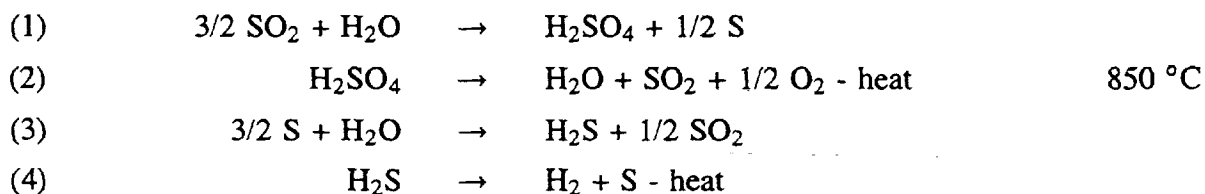


investigated in Germany, Italy, Japan, and the USA. Its theoretical efficiency is 44 %, in practice, however, no higher than 30 % due to difficulties given by material problems, the coupling to the process heat source, and the separation of the gaseous phases. Subjects of investigation at the Research Center Jülich were the “modified AGNES” process with the reaction (4), the reverse Deacon process, conducted in two steps:

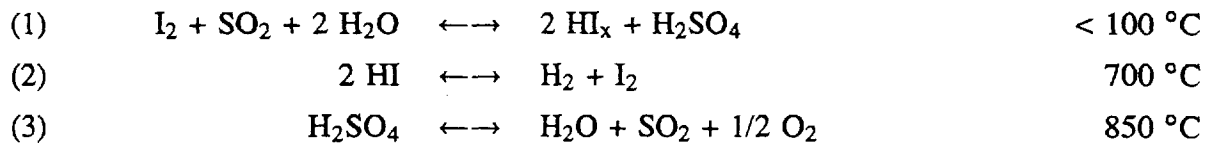


A.2.3. Sulfur Family Processes

Three surviving thermochemical cycles are based on the sulfur family processes which all have in common the thermal decomposition of sulfuric acid at high temperatures. A typical representant is the four steps process:

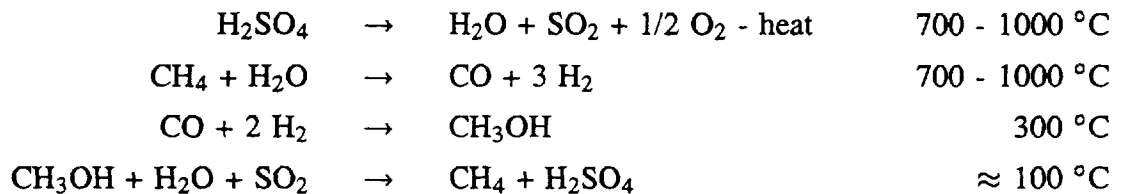


The most considerable potential has the **iodine-sulfur (IS) process** which has been first investigated at General Atomics, San Diego, USA, for many years demonstrating its feasibility and evaluating first chemical engineering flow sheets. The IS process as pursued at JAERI consists of the following three steps:



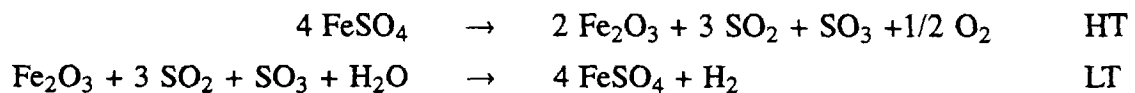
comprising the exothermal water consuming Bunsen reaction, the endothermal decomposition of hydrogen iodide in an electro dialysis cell as the hydrogen producing reaction, and the thermal decomposition of sulfuric acid as the oxygen producing reaction [12]. The decomposition of H_2SO_4 and HI was found to be an expending procedure causing severe corrosion problems. According to analytical studies, an efficiency of 40 - 50 % under optimal operating conditions can be expected [10]. General Atomics gives a figure of 47 % [15]. The IS process was originally designed to be coupled with a high-temperature reactor or a fusion reactor and more recently also with a solar thermal plant. The cycle has been verified on a laboratory scale (1 - 10 NI of H_2 per hour) in Japan and is intended to be later connected to HTTR process heat for demonstration (see also chapter 8).

The **sulfuric acid-methanol process** is given by



with the goals to design and optimize the processing steps and to demonstrate its feasibility on an industrial scale [2].

In the "sulfate" process by



the high-temperature (HT) step is easily selected at $> 980 \text{ K}$, whereas the low-temperature (LT) step results in H_2S and FeS_2 formation rather than H_2 . This brought up the idea to substitute the LT step by an electrolysis step.

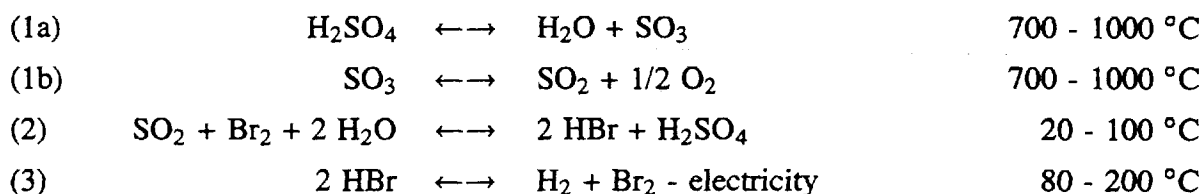
A.3. THERMOCHEMICAL HYBRID CYCLES

The **thermochemical hybrid process** is a combined cycle process with both thermochemical and electrolytic reactions of water splitting. The hybrid process offers the

possibility to run low-temperature reactions on electricity. The expectations for realization of hybrid processes are similar to those for purely thermochemical processes [3]. Various hybrid processes are energetically possible, however, not always feasible. Important criteria are the minimum voltage for the electrolysis step, realizability, efficiency.

A.3.1. Sulfuric Acid Bromine Hybrid Process

The **sulfuric acid-bromine hybrid process** (or "Mark 13") which has been tested at the JRC Ispra, Italy, consists of the reactions:

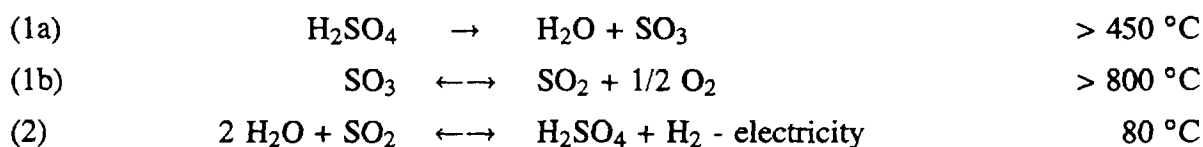


with reaction (3) as the electrochemical step. This cycle using only liquid or gaseous species operated successfully in 1978 in a laboratory scale plant with a hydrogen production rate of 100 l/h over 150 h. An efficient way was found to remove SO₂ by reaction with bromine which was the basis for creating a new flue gas desulfurization process [14]. The efficiency is given as 37 % [15].

A new innovative system is being developed to apply solar energy for the step of HBr production. Concentrated solar radiation is absorbed by bromine vapor to produce bromine atoms which then react with steam at temperatures between 600 and 1000 °C to form HBr and oxygen. A 1 kW solar system was constructed and tested. HBr conversion rates were observed to be 70 % of the theoretical maximum [6].

A.3.2. Sulfuric Acid Hybrid Process

The **sulfuric acid hybrid cycle** (Westinghouse process) is given by the reaction equations

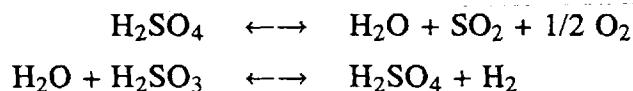


Optimum efficiency is reached with a 65 % concentration of sulfuric acid in water. The weak point is again the decomposition of the sulfuric acid introducing significant corrosion problems. The cycle efficiency is 40 % which has the potential to be increased to 46 % if the electrolysis is conducted in several stages.

The cycle, developed by Westinghouse in 1975, has been experimentally investigated at the Research Center Jülich in close cooperation with JRC Ispra. It has eventually led to a three-compartment electrolysis cell with a hydrogen production rate of 10 NI/h successfully operated in a 600 h test run. Cell conditions were 80 °C at 1.5 MPa [15]. Tube materials

selected have shown an excellent corrosion resistance. The possibility to use direct sunlight for the SO₃ decomposition step was also demonstrated.

The two-step sulfuric acid hybrid process is using in the thermal ($\approx 900\text{ }^\circ\text{C}$) oxygen-producing step the decomposition of sulfuric acid and sulfonic acid in the electrochemical hydrogen-producing step:

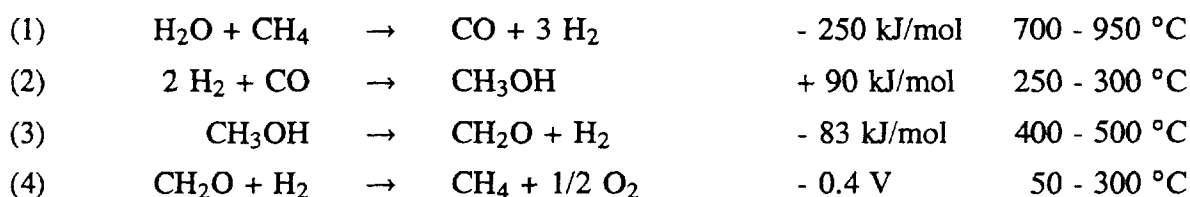


The hybrid process with just two steps is expected to reduce material streams as compared with the above described IS process. The electric energy demand here is a factor of 7 (in reality 3 - 4) lower than in the electrolytic water splitting process.

A.3.3. Hydrocarbon Hybrid Process

Hydrocarbon hybrid processes are promising thermochemical cycles. The hydrogen producing step is typically done by methane splitting connected with the formation of CO.

In the **methane-methanol-methanal process**, the major steps are methane splitting, methanol synthesis, methanal synthesis, and methanal electrolysis, for which the chemical reactions are [1]:

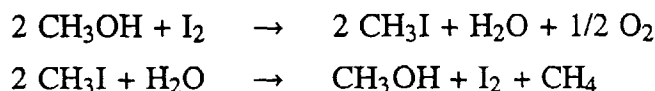


The main energy input is in the steam reforming step (1), which is a well developed and frequently applied technology as is the step (2) of methanol synthesis. Secondary products such as methane and higher hydrocarbons created during the methanol synthesis are considered not significant. The cycle is characterized by a selectively working catalyst and a high reaction rate. The methanal (= formaldehyd) is generally applied on a large-scale in an autothermal operation at about 600 °C by combining exothermal oxidation (methanol + oxygen \rightarrow methanal + water) with endothermal dehydration (methanol \rightarrow methanal + water). The electric energy required in the methanal electrolysis in step (4) is about a third of that needed in the direct electrolysis of water. In contrast to the previous steps, this process step (4) is not well known and needs further development work. Advantages of the cycle are that all reaction partners are in either liquid or gaseous state and neither one is exotic nor poisonous. Recuperation, i.e. the reuse of released heat energy, is significant for an economic process. Anticipating design improvements, the above process is expected to achieve an efficiency of 51 % [1].

The cycle processes “methane-methanol” and “methanal-methanol” based on only three and two, respectively, main reactions require a larger electricity input. The process

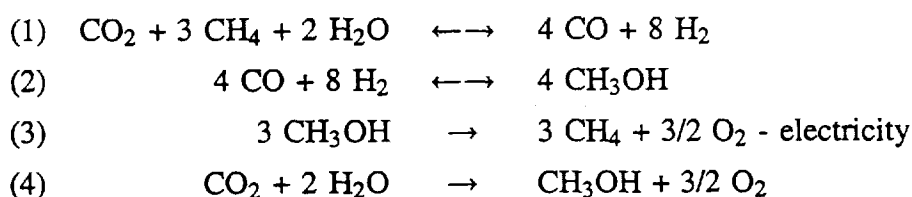
“sulfonic acid-sulfuric acid” consumes the least electricity, but is probably plagued by severe material problems. Other processes such as “acetone-propane-propylene” and “quinone-hydroquinone” need more instrumental effort [1].

The **methane production**, reactions (3) and (4), could also be made by means of methanol plus iodine



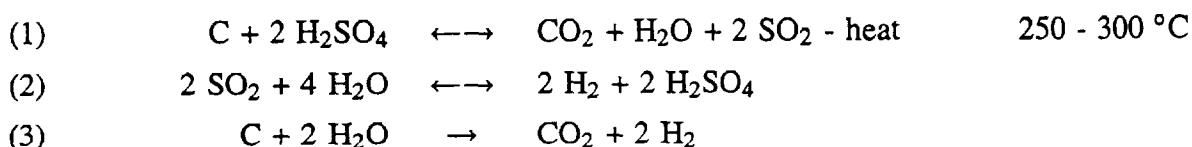
with a conversion rate achieved in experiments of up to 50 % of methane [15].

Production of methanol is made in the following hybrid cycle



The carbon source CO_2 could be taken from the waste gas of coal power plants. This cycle represents a good candidate for the production of a liquid energy carrier with nuclear heat as well [15].

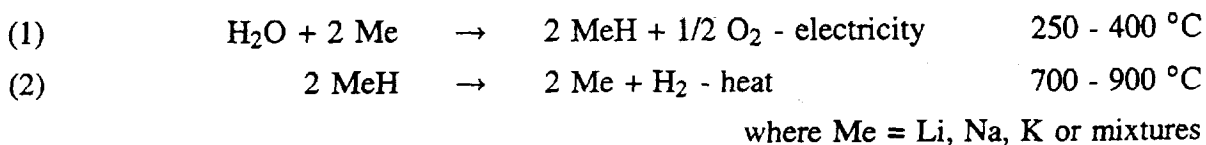
A combined procedure for the **co-production of hydrogen and electricity** from water splitting and coal has been proposed with the following reaction system



The fuel coal, represented by “C”, is oxidized with chemically bound oxygen. The heated combustion gases are routed to a gas turbine to run the electrolysis step. The SO_2 and H_2O are applied in a Westinghouse cycle. An optimum efficiency is seen at 57 % [15].

A.3.4. Metal-Metal Hydride Hybrid Process

In the metal-metal hydride system, the following reactions occur with “Me” representing an alkali metal [15]



Oxygen gas is developed while the hydrogen is bound into the metal. A few tests were conducted with the **lithium hybrid process**, which has been developed at the RWTH Aachen, Germany. Out of some 40 candidate materials for the cell membrane, TiNi alloys were shown to be corrosion resistant for more than 500 h under electrolysis conditions. A thermodynamic analysis indicates an efficiency of 45 %, if hydrogen at a pressure of 4 MPa is provided [15].

Using experience with sodium from the breeder technology, the RWTH Aachen has investigated the **sodium cycle**, $Me=Na$, in 1988/89 with a promising > 50 % overall efficiency. The high-temperature step was operated continuously on a laboratory scale. Cathodic membrane material problems were encountered in the electrochemical step [7].

The Me/MeH hybrid cycle offers an interesting possibility of hydrogen production in connection with a high-temperature gas-cooled reactor.

REFERENCES TO APPENDIX A

- [1] BARNERT, H., Anmerkungen zur thermochemischen Produktion von Wasserstoff aus Wasser mittels Hochtemperaturreaktor-Wärme, Report Jül-1660, Research Center Jülich (1980).
- [2] BARNERT, H., Wasserstoff aus Wasser + HTR-Wärme, KFA Annual Report 1974, Research Center Jülich (1975) 25-30.
- [3] BECKURTS, K.-H., DIETRICH, G., Projekt Fernwärme Versorgung für Millionen-Städte, Bild der Wissenschaft 13 (1976) January 64-70.
- [4] FRIE, W., Thermochemische Kreisprozesse zur Wasserstoff-Erzeugung, Wasserstoff als Energieträger, (Status Seminar, Würzburg, 1995), Projektträger Biologie, Energie, Ökologie, Research Center Jülich (1995) 47-60.
- [5] FUNK, J.E., Hydrogen Production, Tutorial during the 10th World Hydrogen Energy Conf., Cocoa Beach, USA, June 19, 1994.
- [6] HEATON, H., Production of HBr from Bromine and Steam for Off-Peak, World Wide Web, <http://www.eren.doe.gov/hydrogen/hbr.htm>, US Department of Energy (1997).
- [7] HERZOG, F., Development of the Metal/Metal Hydride Process, in: IEA, Implementing Agreement for a Programme of Research and Development on the Production of Hydrogen from Water, Annex IX: Hydrogen Production, Technical Report, Document HUF-4, Research Center Jülich (1990) 99-133.
- [8] KNOCHE, K.F., Stand der Arbeiten zur Wasserstoff-Erzeugung mit nuklearer Prozeßwärme, Chem.-Ing.-Tech. 49 (1977) 238-242.
- [9] LUNDBERG, M., ROSEN, E., Model Calculations on Some Thermochemical Water Splitting Processes, Hydrogen Production, (2nd IEA Technical Workshop, Jülich, FRG, 1991), STRUCK, B.D. (Ed.), Implementing Agreement for a Programme of Research and Development on the Production of Hydrogen from Water, Document HUF-6, Research Center Jülich (1991) 87-98.
- [10] ONUKI, K., et al., Studies on Water Splitting Hydrogen Production, (3rd JAERI Symp., Oarai, 1996), Proc. JAERI-Conf 96-010, Japan Atomic Energy Research Institute (1996) 462-474.
- [11] PESCHKA, W., Liquid Hydrogen: Fuel of the Future, Springer-Verlag Wien New York (1992).

- [12] SHIMIZU, S., ONUKI, K., NAKAJIMA, H., Bench-Scale Studies of the Iodine-Sulfur Process, Hydrogen Production, (2nd IEA Technical Workshop, Jülich, FRG, 1991), STRUCK, B.D. (Ed.), Implementing Agreement for a Programme of Research and Development on the Production of Hydrogen from Water, Document HUF-6, Research Center Jülich (1991) 49-62.
- [13] STEINFELD, A., et al., Solar-Processed Metals as Clean Energy Carriers and Water-Splitters, (11th World Hydrogen Energy Conf., Stuttgart, FRG, 1996), VEZIROGLU, T.N., et al., Hydrogen Energy Progress XI, International Association for Hydrogen Energy (1996) 601-609.
- [14] VAN VELZEN, D., Desulphurization and Denoxing of Waste Gases Producing Hydrogen as a By-Product, Hydrogen Production, (2nd IEA Technical Workshop, Jülich, FRG, 1991), STRUCK, B.D. (Ed.), Implementing Agreement for a Programme of Research and Development on the Production of Hydrogen from Water, Document HUF-6, Research Center Jülich (1991) 99-111.
- [15] WEIRICH, W., et al., Thermochemical Processes for Water Splitting – Status and Outlook, Nucl. Eng. Des. **78** (1984) 285-291.
- [16] YOSHIDA, K., Hydrogen Production by UT-3 Thermochemical Water Decomposition Cycle, Hydrogen and Clean Energy (Int. Symp., Tokyo, 1995), NEDO (1995) 39-46.

**NEXT PAGE(S)
left BLANK**