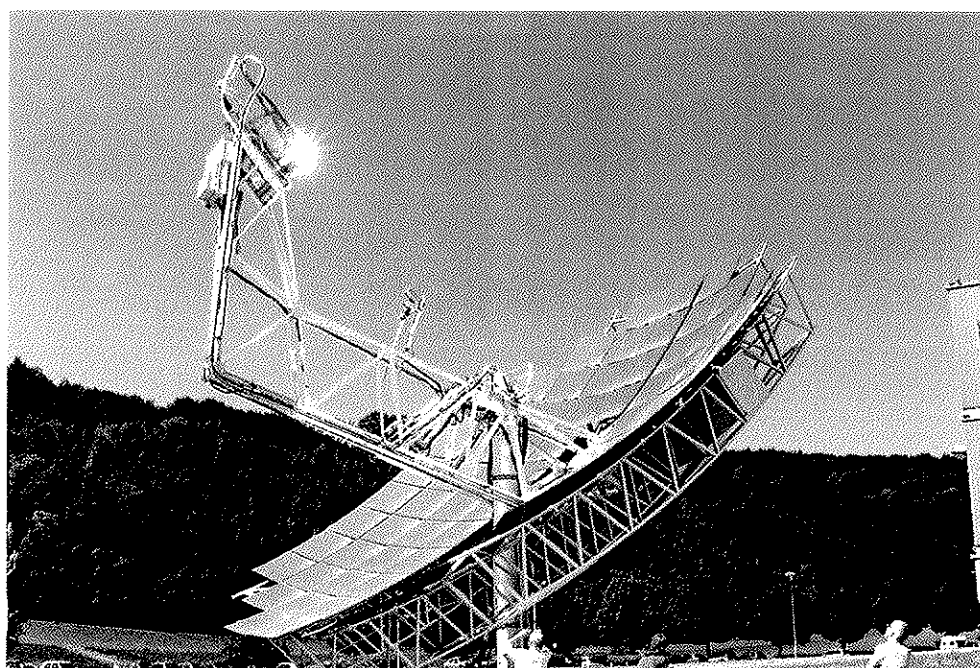


International Workshop on HIGH-TEMPERATURE SOLAR CHEMISTRY

August 17, 1995

Paul Scherrer Institut, CH-5232 Villigen, Switzerland

Notes



Preface

An international workshop on High-Temperature Solar Chemistry was held at the Paul Scherrer Institut in Villigen, Switzerland, on August 17, 1995. This event contributed to the international collaboration R&D Program carried out under the umbrella of the SolarPACES Agreement of the International Energy Agency (IEA).

The present notes contain documentation material (abstracts and viewgraphs), presented by the invited speakers. More than 60 scientists, engineers, and students from 7 countries (Australia, France, Germany, Israel, Japan, Switzerland, and the United States) participated in the workshop.

The organizers express their gratitude to all speakers and participants for the fruitful and motivating discussions and look forward to future activities.

A. Steinfeld and P. Kuhn
Chairmen of the Workshop

PAUL SCHERRER INSTITUT



"Solar Chemistry: Putting Solar Energy in Motion"

Prof. R. Palumbo
PSI-Seminar, 6.7.1995

Contents

		Page
1	Program of Workshop	7
2	Documentation	9
•	Why Solar Chemistry ?	Dr. Paul Kesselring Paul Scherrer Institut Switzerland 11
•	Hydrogen Sulfide and Solar Energy in the 21st Century	Prof. Edward A. Fletcher University of Minnesota USA 26
•	A New Energy Global System: Combination of Solar Energy and Fossil Fuel Energy Using Metal Oxides	Prof. Yutaka Tamaura Tokyo Institute of Technology Japan 43
•	Reactivity of Solids - Basic Aspects for the Chemical Conversion of High-Temperature Solar Energy	Prof. H.R. Oswald University of Zürich Switzerland 60
•	New Opportunities for High-Temperature Solar Chemistry	Dr. Michael Epstein Weizmann Institute of Science Israel 85
•	The Use of Metal Oxides in High- Temperature Solar Processing	Prof. Robert D. Palumbo Valparaiso University USA 112
•	Solar-Assisted Chemical Processes - A Way Out of the Fossil Energy Systems?	Prof. Armin Reller University of Hamburg Germany 128
•	Solar Thermal Processes Using Metal Carbides and Nitrides	Prof. Jean P. Murray Portland State University USA 136
•	Approaches to High-Temperature Solar Destruction of Hazardous Wastes	Dr. Karl H. Funken DLR-Köln Germany 154
•	High-Pressure Solar Ammonia Dissociation	Andreas Luzzi Australian National University Australia 180
3	List of Participants	195

PROGRAM

Morning Session

09:00	- <i>Opening</i> -	Prof. Alexander Wokaun Paul Scherrer Institut Switzerland
09:05	"Why Solar Chemistry?"	Dr. Paul Kesselring Paul Scherrer Institut Switzerland
09:30	"Hydrogen Sulfide and Solar Energy in the 21st Century"	Prof. Edward A. Fletcher University of Minnesota USA
10:00	"A New Energy Global System: Combination of Solar and Fossil Fuel Energy Using Metal Oxides"	Prof. Yutaka Tamaura Tokyo Institute of Technology Japan
10:30	"Reactivity of Solids - Basic Aspects for the Chemical Conversion of High- Temperature Solar Energy"	Prof. H.R. Oswald University of Zürich Switzerland
11:00	- <i>Coffee Pause</i> -	
11:15	"New Opportunities for High- Temperature Solar Chemistry"	Dr. Michael Epstein Weizmann Institute of Science Israel
11:45	"The Use of Metal Oxides in High- Temperature Solar Processing"	Prof. Robert D. Palumbo Valparaiso University USA
12:15	"Solar-Assisted Chemical Processes - A Way Out of the Fossil Energy Systems?"	Prof. Armin Reller University of Hamburg Germany
12:45	- <i>Lunch</i> -	

Afternoon Session

14:00	"Solar Thermal Processes Using Metal Carbides and Nitrides"	Prof. Jean P. Murray Portland State University USA
14:30	"Approaches to High-Temperature Solar Destruction of Hazardous Wastes"	Dr. Karl H. Funken DLR-Köln Germany
15:00	"High-Pressure Solar Ammonia Dissociation"	Andreas Luzzi Australian National University Australia
15:30	- <i>Visit to PSI Solar Facilities & Coffee Pause</i> -	
17:00	Debate: "Solar Chemistry beyond the Year 2000 - Potentials, Possibilities, and Applications"	
18:00	- <i>Closing</i> -	

Documentation

Abstracts and Viewgraphs of Invited Speakers

Why Solar Chemistry?

Paul Kesselring
Paul Scherrer Institut
CH-5232 Villigen PSI
Switzerland

Why solar chemistry? *Sponsors* might want to get a convincing answer to this question before funding one of our projects. This here, however, is the first contribution to a specialists' meeting. So why this title!?

Before starting for a busy day, full of technical and scientific discussions, it might be worthwhile to lean back for a moment and remind ourselves why solar chemistry is important. The topics, I would like to touch in this connection, have all to do with the substitution of fossil resources by renewables and, therefore, are connected with the modern catchword "sustainability". The questions related to these topics are:

- Why not an all electric energy system?
- Why is it so difficult to replace oil in some of its most valuable functions?
- Why solar **thermal** chemistry?

Emphasis will be put on the longterm importance of solar chemistry for future energy systems. However, other issues such as "raw materials" or "waste treatment and recycling" are different aspects of the same problem area and should not be forgotten.



IEA-SolarPACES International Workshop

on

High Temperature Solar Chemistry

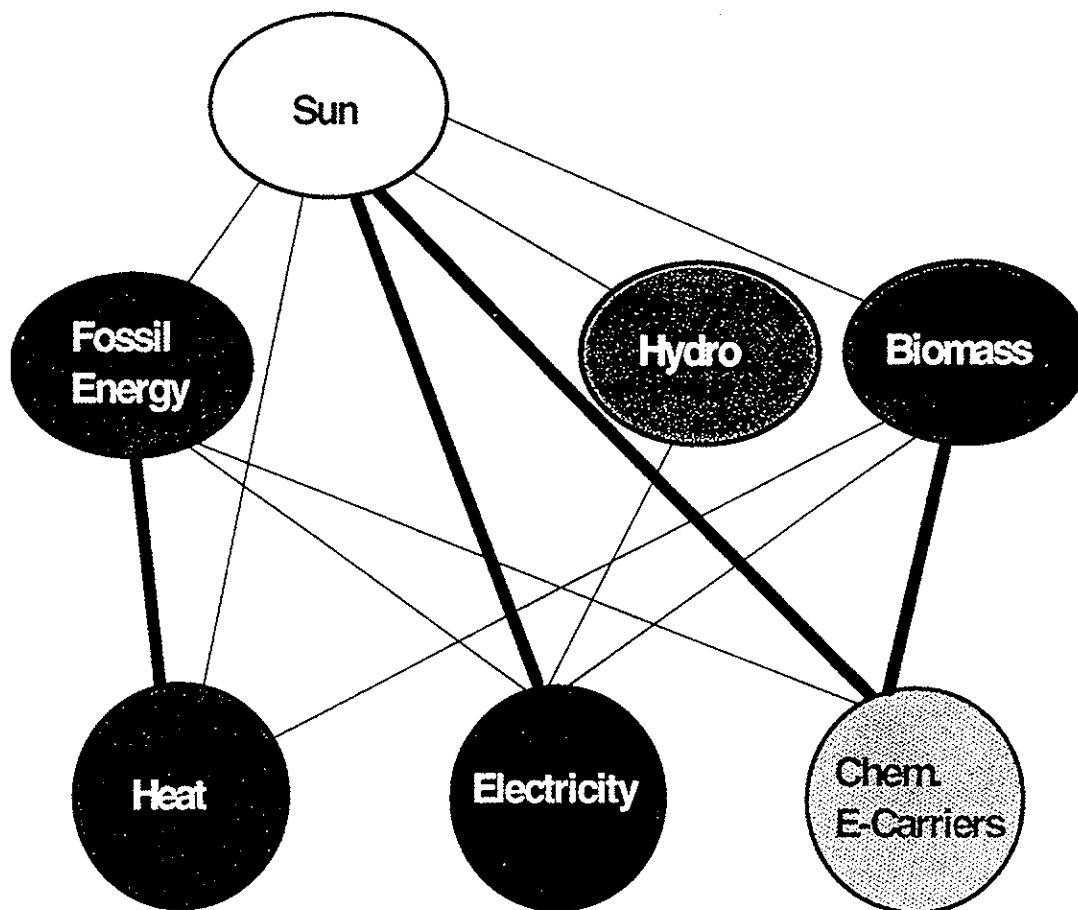
PSI, August 17, 1995

Why Solar Chemistry?

P. Kesselring, PSI

- Why this title?!
- Sustainability and Substitution of oil:
Energy, commodities, ..., ...
- Energy
 - Why not all electric?
 - Why is oil so difficult to replace?
 - Why solar thermal chemistry?
- Final remarks

Energy and Sustainable Development



Energy System

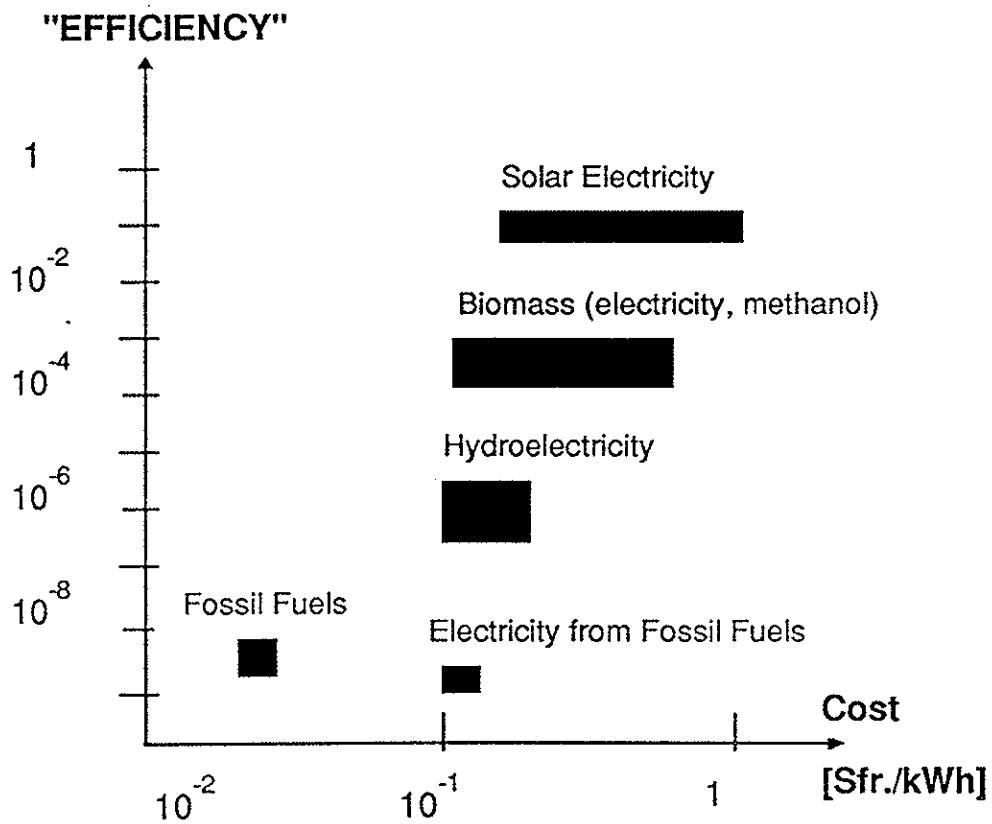
- fossil energies still dominant
- substitution unavoidable in the long term

PSI Contributions

- clean and efficient combustion
- laserdiagnostics
- BIOMETH
- thin solar cells
- solar hydrogen



The Sun as a Primary Energy Source





WHY NOT "ALL ELECTRIC" ?

- **STORAGE OF POTENTIAL ENERGY REQUIRES BATTERIES**

- **COMPARED TO GASOLIN:**
 - **ENERGY DENSITY 2 ORDERS OF MAGNITUDE SMALLER**
 - **POWER DENSITY (ENERGY STORAGE + ENGINE) AT LEAST 5x SMALLER FOR ELECTRIC SYSTEM**
 - **CHARGING TIMES: ORDERS OF MAGNITUDE LONGER FOR BATTERIES ($10^2 - 10^3$)**

- **CAN YOU IMAGINE A "JUMBO-JET" FLYING WITH BATTERIES ?!**
RATHER: SYNTHETIC FUELS + FUEL CELLS

Flow of Matter and Power

- **Gas station for cars:**

**1 l/s of gasolin \Rightarrow > 30 MW
(chemical)**

- **River powerstation Eglisau:**

River Rhein

**$> 300'000$ l/s, 10 m \Rightarrow ≈ 30 MW
(electric)**



THE IMPORTANCE OF STORAGE AND TRANSPORTATION OF ENERGY

OIL

PUMPING FROM GROUND

TRANSPORTATION

STORAGE

RAFFINATION

DISTRIBUTION

STORAGE

DISTRIBUTION (RETAIL)

STORAGE (END USER)

FINAL USE

SOLAR ENERGY

RADIATION ON SURFACE

TRANSPORT

RECEIVER

ELECTRICITY

STORAGE ? ?

TRANSPORT

DISTRIBUTION

STORAGE

FINAL USE

FINAL USE



STORE POTENTIAL, NOT KINETIC ENERGY !

KINETIC ENERGY

FLY-WHEEL

BULLET

EL. CURRENT

HEAT

RADIATION

DIFFICULT TO STORE

POTENTIAL ENERGY

HYDRO-RESERVOIR

GUN POWDER

SEPARATED CHARGES

CHEMICAL BOND

EASY TO STORE

POTENTIAL \leftrightarrow FORCE

FORCES (MICROSCOPIC LEVEL)

GRAVIATION	10^{-6}	(μeV)
VAN DER WAALS	10^{-3}	
HYDROGEN BOND	10^{-1}	
COVALENT BOND ^{*)}	1	(eV)
IONIC BOND	1	
NUCLEAR FORCES	10^6	(MeV)

^{*)} TYPICALLY 418 kJ/Mol (100 k Cal/Mol)
or 4.3 eV

<p>→ CHEMICAL STORAGE IS THE LONG-TERM STORAGE METHOD</p>

PROBLEMS OF A POST FOSSIL ERA

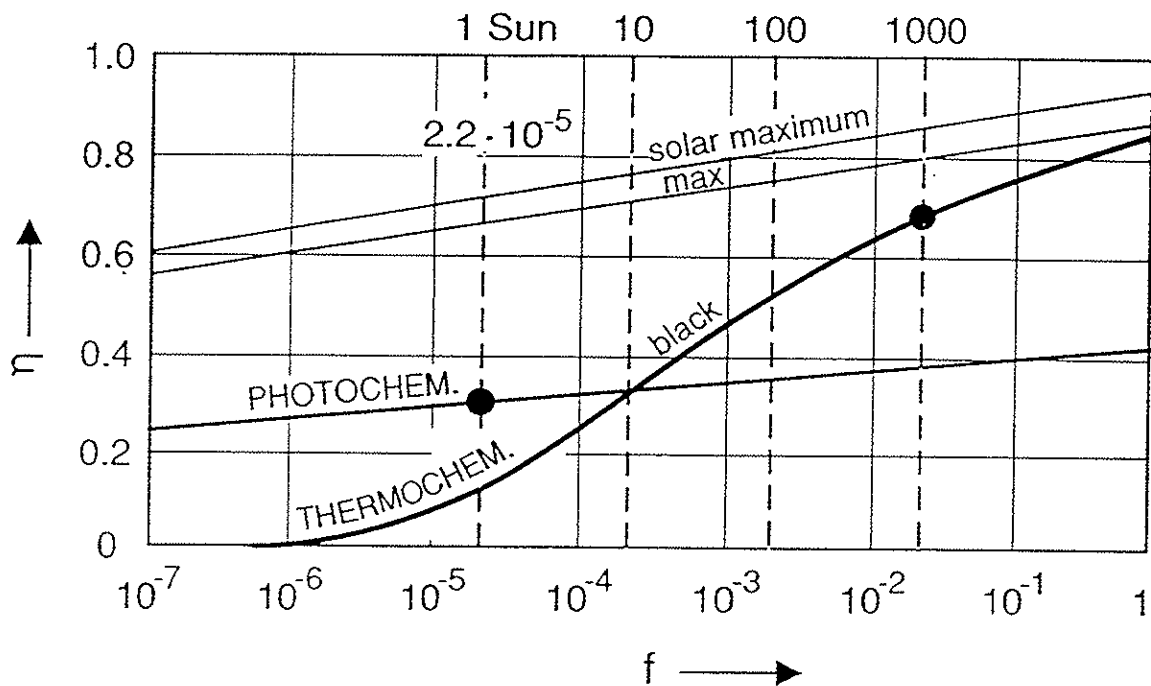
- **PRIMARY ENERGY SOURCES:**
 - **RENEWABLES (SOLAR)**
 - **NUCLEAR ENERGY (FISSION, FUSION)**

- **"PRODUCTS":**
 - **SOLAR RADIATION**
 - **HEAT**
 - **ELECTRICITY**

- **CONVERSION TO CHEMICAL ENERGY:**
 - **RADIATION** → **PHOTOCHEMISTRY**
 - **HEAT** → **THERMOCHEMISTRY**
 - **ELECTRICITY** → **ELECTROCHEMISTRY**

Photochemistry and Thermochemistry

Theoretical limits of efficiencies



picture according to R. Sizmann

Advantages and Disadvantages

	Thermochemistry	Photochemistry
Advantages	High efficiency possible	Low temperature
Disadvantages	Direct radiation only	Efficiency more limited

Solar High Temperature Chemistry

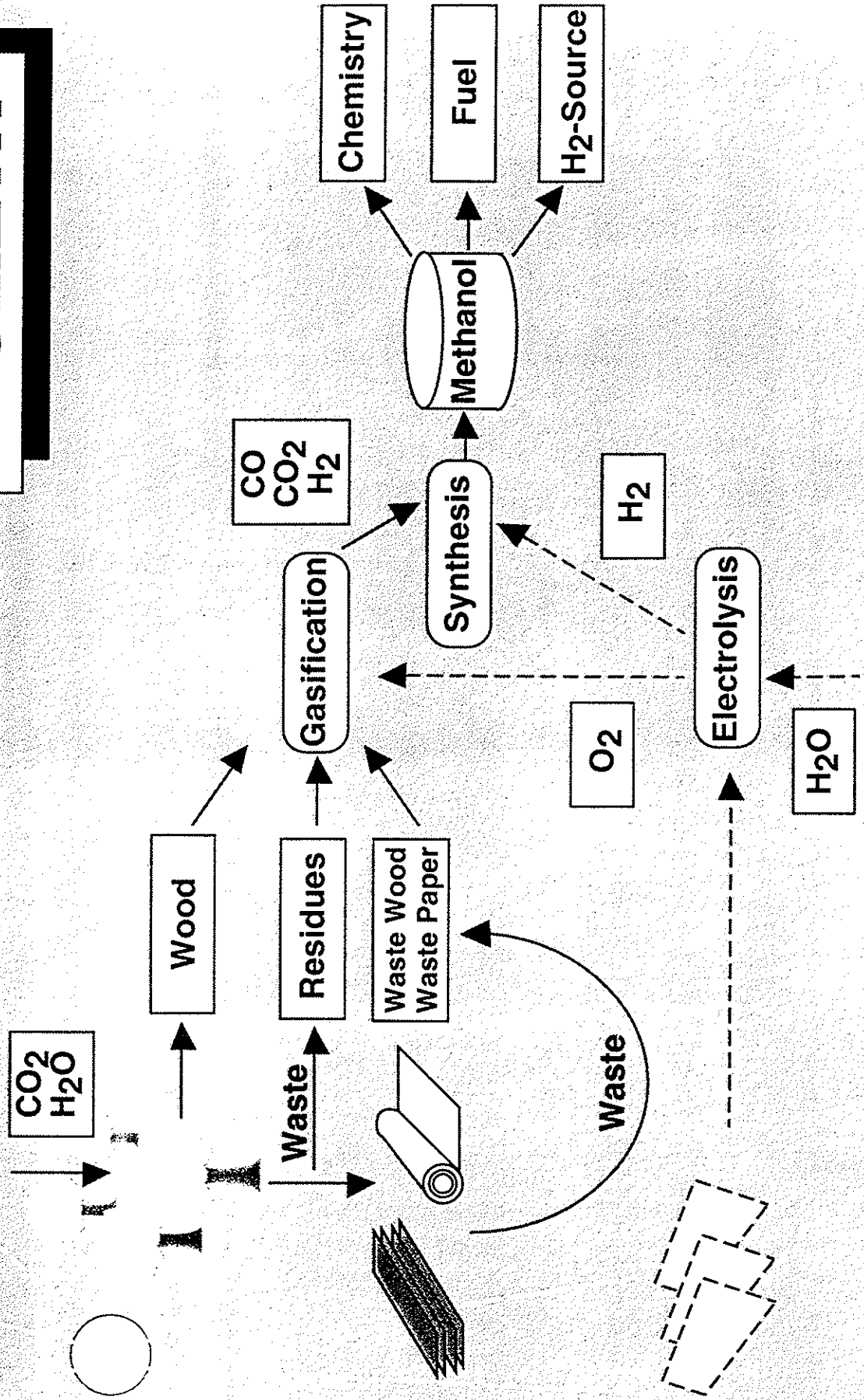
- **Replace "fossil fire" by "solar fire" in conventional thermal processes**

⇒ **Failure ahead !**

- **Solar specific processes**
 - **minimize material**
 - **short time constant of first stage**
 - **direct absorption/reaction**
 - **combined thermo-/photochemical reactions**



BIOMETH



Hydrogen Sulfide and Solar Energy in the 21st Century

Edward A. Fletcher
Department of Mechanical Engineering
University of Minnesota
Minneapolis, MN 55455, USA

Sulfur is present in all the oil and gas we refine. Hydrogen sulfide is a disagreeable toxic waste. It's produced in sweetening fossil fuels. It should be regarded as a valuable resource. Many gas wells contain so much they cannot be used now. Many, all over the world, contain more hydrogen sulfide than hydrocarbons. If the hydrogen associated with sulfur in U.S. and Canadian refining operations had been recovered rather than oxidized to water in 1979, for example, it could have provided the heating value of 17 million barrels of gasoline. It would have had even greater value as a feedstock for the chemical and petroleum industries. A study we did eleven years ago (Diver and Fletcher) suggested that, if hydrogen sulfide were assigned a value of zero (as an industrial waste it has a substantial negative value), a solar energy process could be marginally competitive with the Claus process which is now used to deal with it. Less costly energy from any current conventional source would provide a strong, profitable alternative, now, if it were used to recover both hydrogen and sulfur without introducing air. The Claus process uses air to burn the hydrogen to water. The nitrogen becomes a pollutant laden stack gas which is very costly to clean up. When current environmental constraints are met, the cost of the clean up unit alone cannot usually be recovered from the sale of the sulfur.

Previous studies of hydrogen sulfide thermolysis were limited to upper temperatures of about 1200K. There is an important thermodynamic advantage that would be realized by operating at the higher source temperatures easily achievable with highly concentrated solar energy. That thermodynamic advantage exists regardless of the energy source. One can show [1] that the maximum energy and conversion efficiencies of endothermic processes are related, by Carnot's law, to the temperature at which the process heat is taken up. That means that the higher the tem-

perature of the reactor the lower will be the amount of high temperature process heat required to split a mole of hydrogen sulfide. Moreover, the fraction of the hydrogen sulfide that is converted will be greater. There will be less hydrogen sulfide to separate from the products and recycle. Thus, there will be fewer losses associated with heat exchangers, separators, and all the other components of a system.

We have already done several studies, analytical and experimental, of solar thermolysis [2]. We got very high yields and conversions in experiments at temperatures ranging to about 1800K. High temperature thermolysis in the absence of air can become an important and profitable successor to the Claus process. In a transition period its successor might well be supplied by conventional energy sources; Claus plants should be phased out with the emergence of more profitable and more environmentally benign alternatives. After that, as conventional energy sources are depleted and become more costly, solar can provide a credible alternative. In addition it will make vast reserves of fuels with increasingly high sulfur content profitable.

Thus solar hydrogen sulfide treatment has a strong potentiality for giving credibility- for providing an entree to other solar industrial thermochemical processes.

[1] E.A. Fletcher and R. Moen, *Science* **197**, 1050 (1977).

[2] R.B. Diver and E.A. Fletcher, *Energy* **10**, 831 (1985).

Hydrogen Sulfide and Solar Energy in the 21st Century

Hydrogen Sulfide Thermolysis

Jon Noring

Richard Diver

Todd Kappauf

Robert Palumbo

Jean Murray

Kent Scholl

Electrolysis and Solarthermal Electrolysis

Kirk Nygren

Aldo Steinfeld

William Smyrl

Radoslav Atanasoski

**Table 1 - World Oil Reserves by Region,
1980 and 1989**

Region	Oil Reserves		Share of 1989	Reserves Remaining at 1989
	1980 (billion barrels)	1989	Reserves (percent)	Production Rate (years)
Middle East	362 70	660	65	110
Latin America		125	12	51
Soviet Union & East. Europe	66	60	6	13
Africa	55	59	6	28
Australia	40	47	5	20
North America	39	42	4	10
Western Europe	23	18	2	13
TOTAL	655	1,011	200	44

Source: British Petroleum, *PB Statistical Review of World Energy*
(London: various years)

Global Hydrogen Sulfide Content, % by Weight^a

Location	Hydrogen Sulfide, %
France (Lacq)	16
Germany (Varnhom)	22
Canada (Harmatten, Alberta)	54
Canada (Panter River, Alberta)	70
Canada (Bearberry, Alberta)	90
USA (Smackover, Mississippi)	25-45
Astrakhan (former USSR)	23
China (Zhaolanzhuang)	60-90

^aT. Kappauf, J.P. Murray, R. Palumbo, R.B. Diver, and E.A. Fletcher, *Energy* **10**, pp. 119-1137 (1985).

CONCLUSIONS

The diverse attack on hydrogen sulfide to obtain two salable products is very striking. Every year a large amount of potential resource is being wasted and there is no doubt it should be stopped. The success in the development of a suitable technology for the production of hydrogen and sulfur will signify the attainment of the triple objectives of waste minimization, resource utilization and environmental pollution reduction.

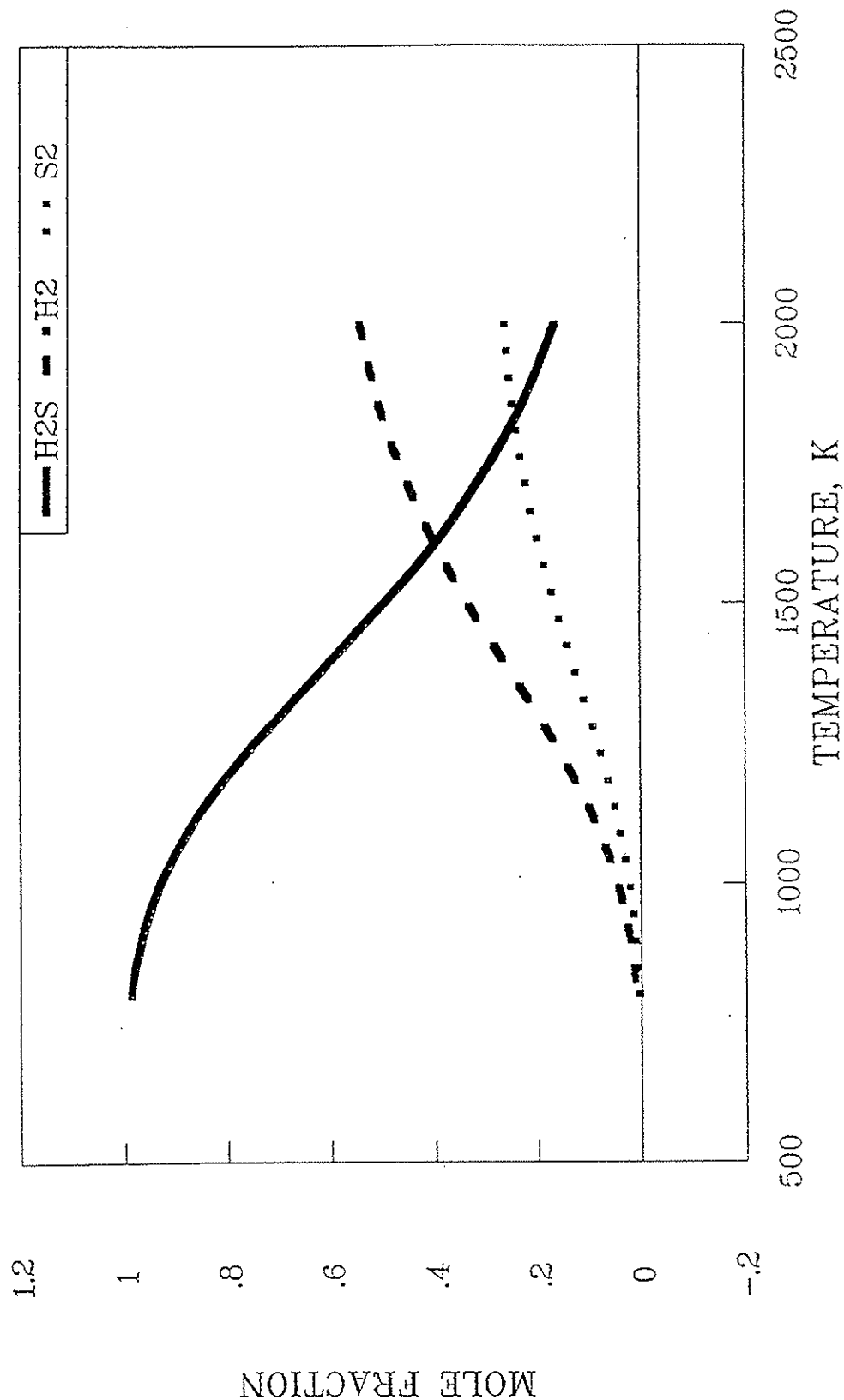
J. Zaman, A. Chakma, *Fuel Processing Technology* **41**, pp. 159-198 (1995).

**Table 1 - Thermal Decomposition of Hydrogen Sulfide
Using Different Types of Reactors**

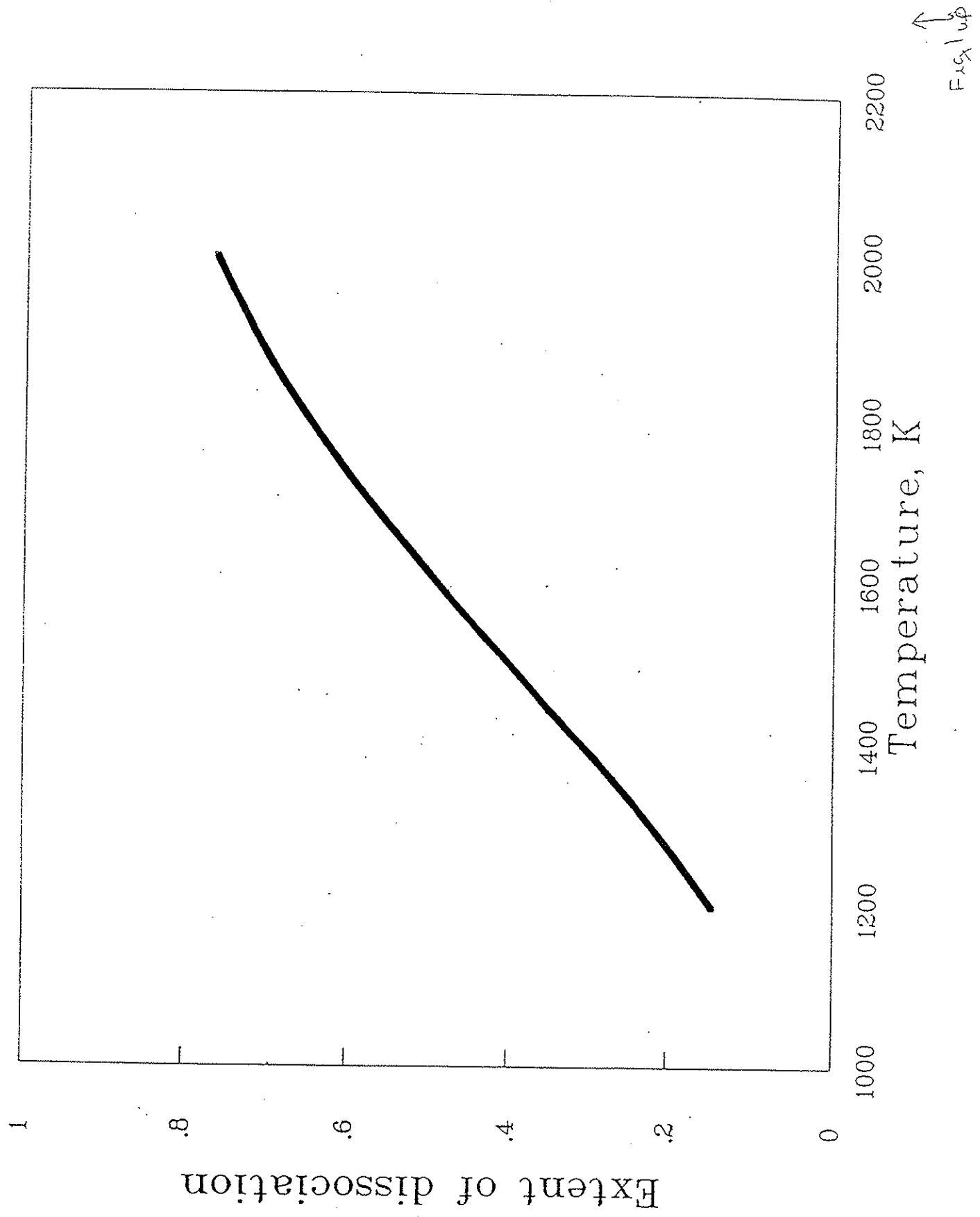
Type of Reaction System [References]	Operating Variables	Important Results
Tubular Reactor [22]	873-1133 K, pressure 131-314 kPa, noncatalytic	Kinetic studies were carried out for thermal decomposition
Tubular Reactor [19,25]	1013-1133 K, pressure 103-314 kPa MoS ₂ catalyst	MoS ₂ catalyst attains stable activity at 65% of the initial value. Hougen Watson Type rate equations developed. Equilibrium conversion matched the thermodynamic data
Tubular Reactor [18,20,21]	800-1260 K, catalysts silica, cobalt molybdate and 1% presulfided Pt 1230 K, 13-50 kPa, Al ₂ O ₃ catalyst	A detailed study of the thermodynamics and rate processes were made
Tubular Reactor [26]	1230 K, 13-50 kPa, Al ₂ O ₃ catalyst	Single pass conversion of 27% at 1230 K and 13 kPa. A commercial plant with capacity 10 ⁶ m ³ 112/d proposed
Tubular Reactor [63,64]	723-873 K, catalysts: Al ₂ O ₃ , 5% V ₂ O ₅ /Al ₂ O ₃ , 10% V ₂ O ₅ /Al ₂ O ₃ , 5% V ₂ S ₃ /Al ₂ O ₃	Kinetic studies were made
Recirculating Reactor [28]	773-1073 K, pressure 5.3-12.0 kPa, MoS ₂ and WS ₂ catalysts	95% conversion of H ₂ S by continuous removal of S and intermittent removal of H ₂
Recirculating Reactor [29,31]	823 K, 6.0 kPa initial H ₂ S pressure, MoS ₂ and other catalyst formulation	Mechanism studies and promoter effects in catalysts
Recirculating Reactor [27,44,45]	673-1073 K, sulfides of Mo, V, Fe, Cu and Zn as catalyst	The effects of the sulfides on hydrogen evolution were investigated.
Membrane Reactor [33,38]	673-1073 K, sulfides of MoS ₂ catalyst	Conversion twice the equilibrium value obtained

Thermal Diffusion Reactor [43]	Hot wall at 773 K, cold wall at 293-298 K, catalysts used Cr ₂ S ₃ , CoS, NiS and FeS	40% decomposition in 4 h (batch), H ₂ concentration at the top of the column 96%. H ₂ S conversion of 10% obtained while the equilibrium value at 500°C was only 0.6%. Equilibrium shift obtained because of separation of products. The performance evaluated with different catalysts and reactor variables
Thermal Diffusion Reactor [44,45]	Hot wall at 673-1073 K, cold wall at 353-373 K, Catalysts/sulfides used: MoS ₂ , V ₂ S ₃ /FeS, V ₂ S ₃ /Cu ₉ S ₅ , V ₂ S ₃ /ZnS, Fe ₇ S ₈ Fe ₇ S ₈ /MoS ₂ and Fe ₇ S ₈ /NiS _{1.2}	
Solar Reactor [46,46]	Temperature 893-1043 K, catalysts used: Ni-W, Ni Mo, Co Mo and alumina	Cobalt-molybdenum catalyst has the highest activity. A hydrogen yield of 19% was obtained at 770°C and residence time of 0.3 s. Kinetic rate equations were developed
Solar Reactor [48,49]	1000-1700 K, 50.6 kPa	Ceramic materials like ZrO ₂ , Al ₂ O ₃ and mullite appear to be chemically suitable for high temperature reactor. High yields (of the order 0.5) and quench fractions (of the order 0.7) were obtained over a range of temperatures and feed rates

EQUILIBRIUM COMPOSITION OF HYDROGEN SULFIDE(a)



(a) J.E. Noring and E.A. Fletcher, Energy 8, 247(1983)



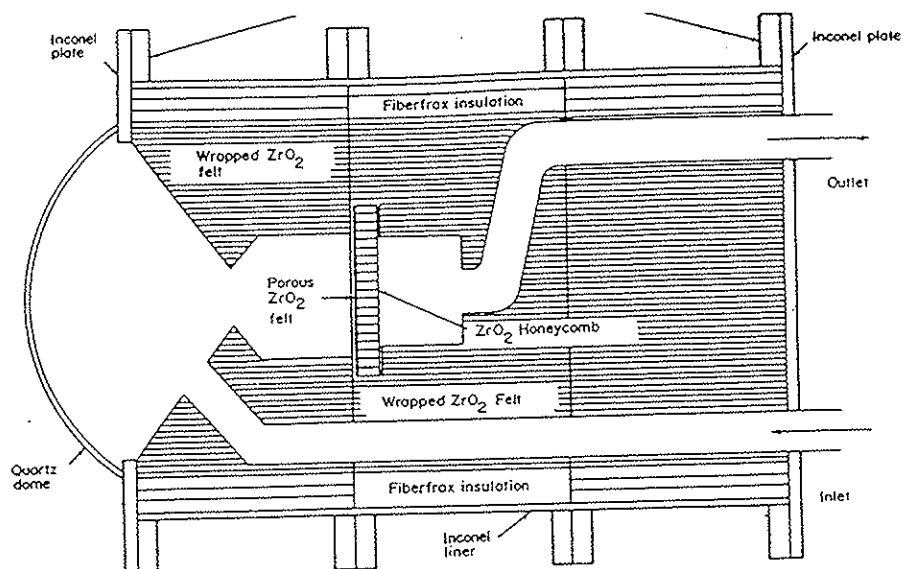


Fig. 2. Schematic diagram of reactor 1.

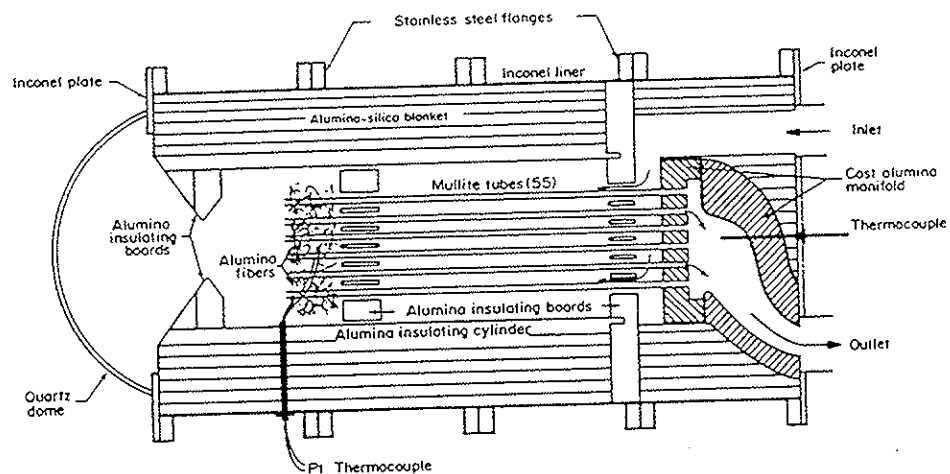
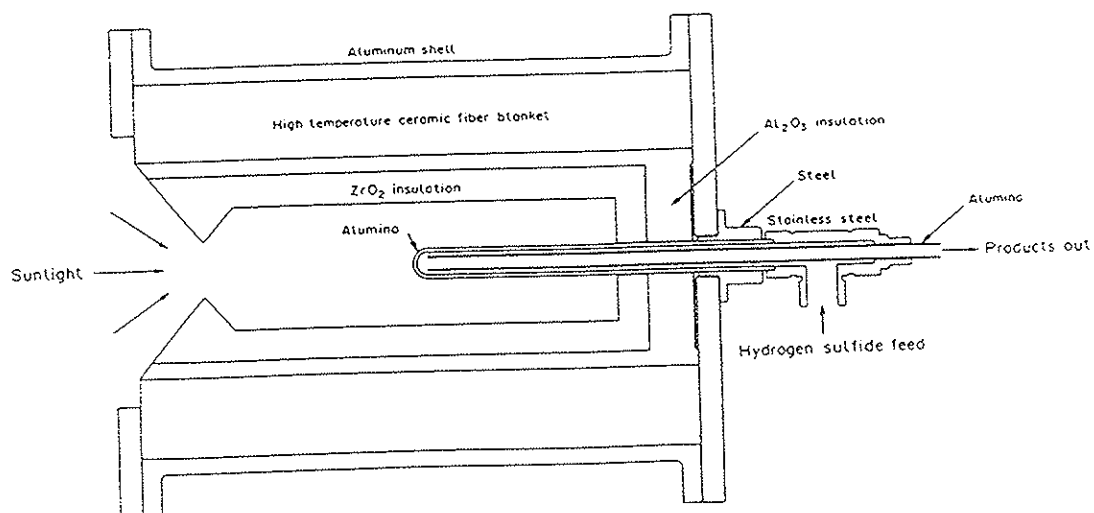


Fig. 3. Schematic diagram of reactor 2.

Fig. 1. Reactor for the solar thermolysis of H_2S .

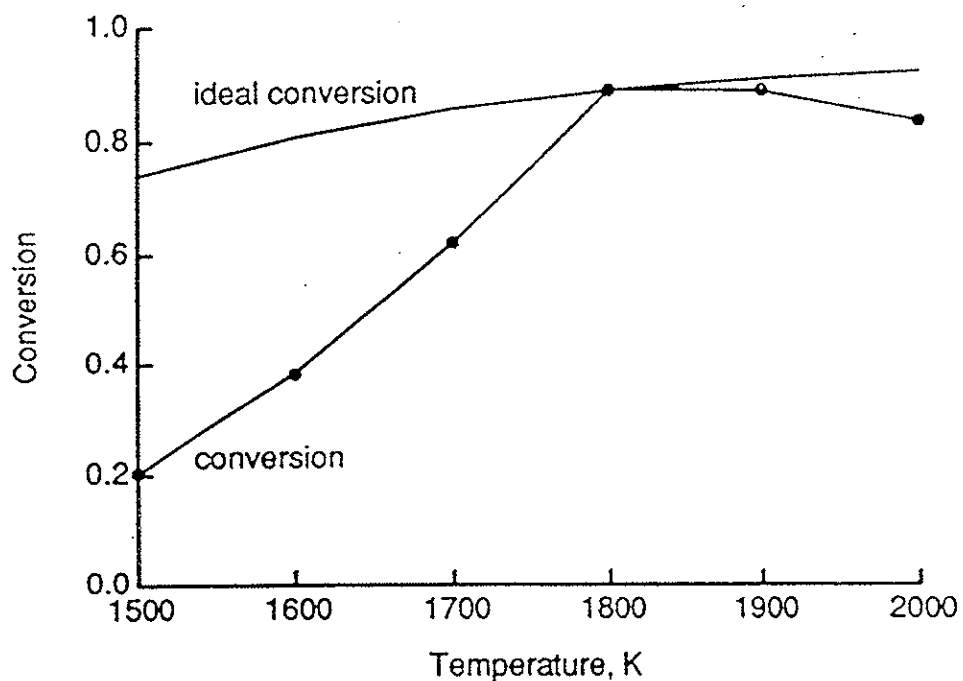
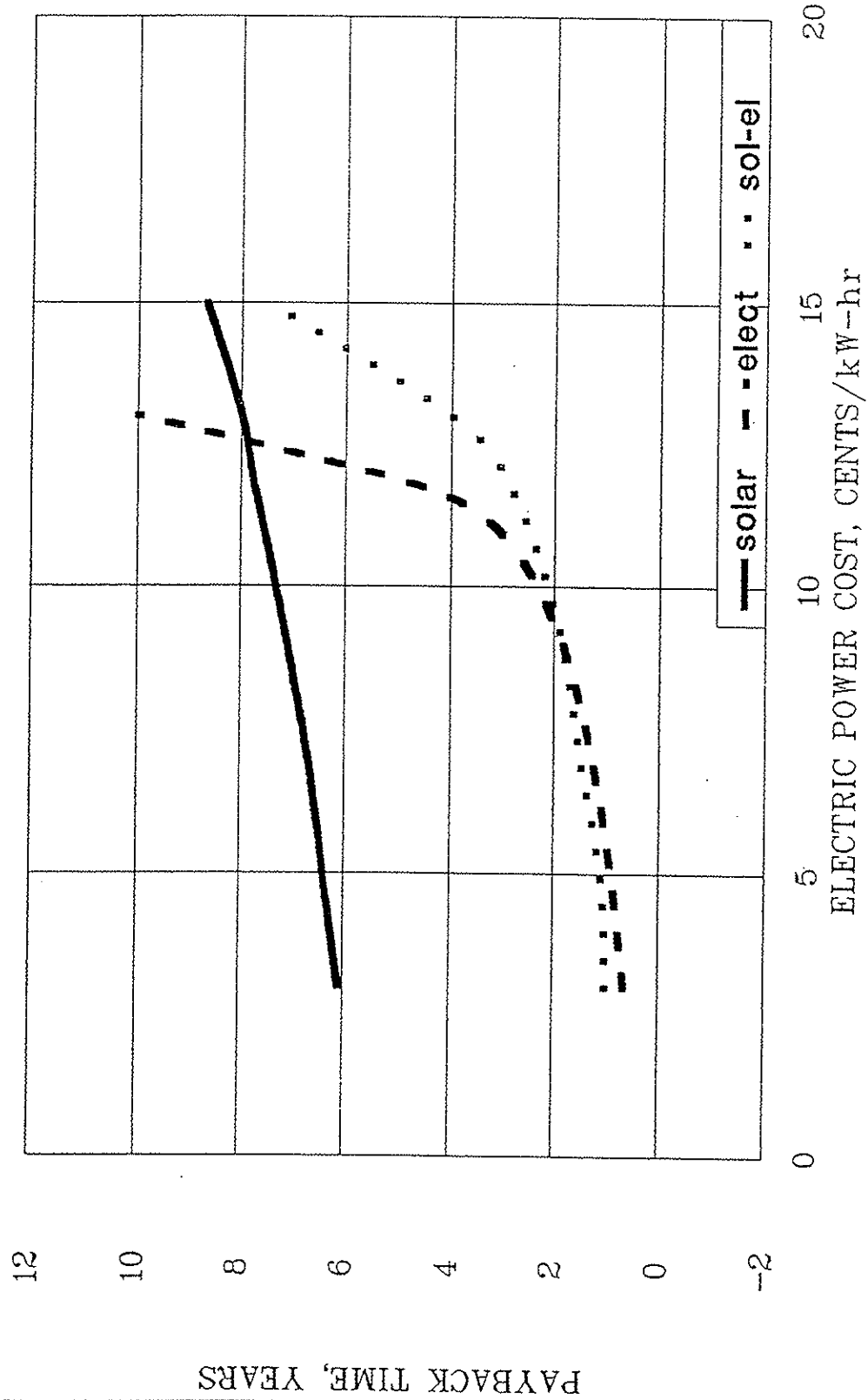
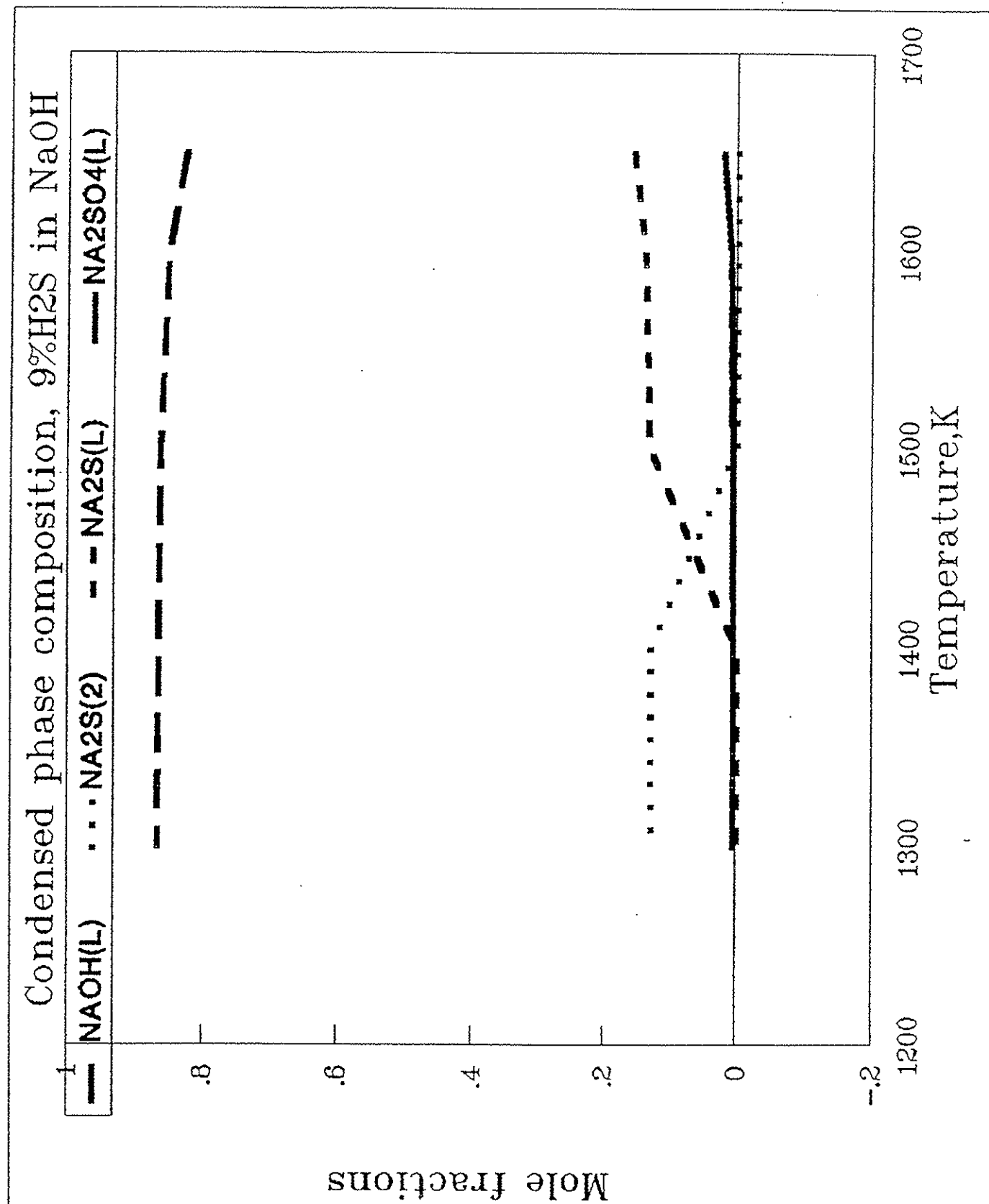


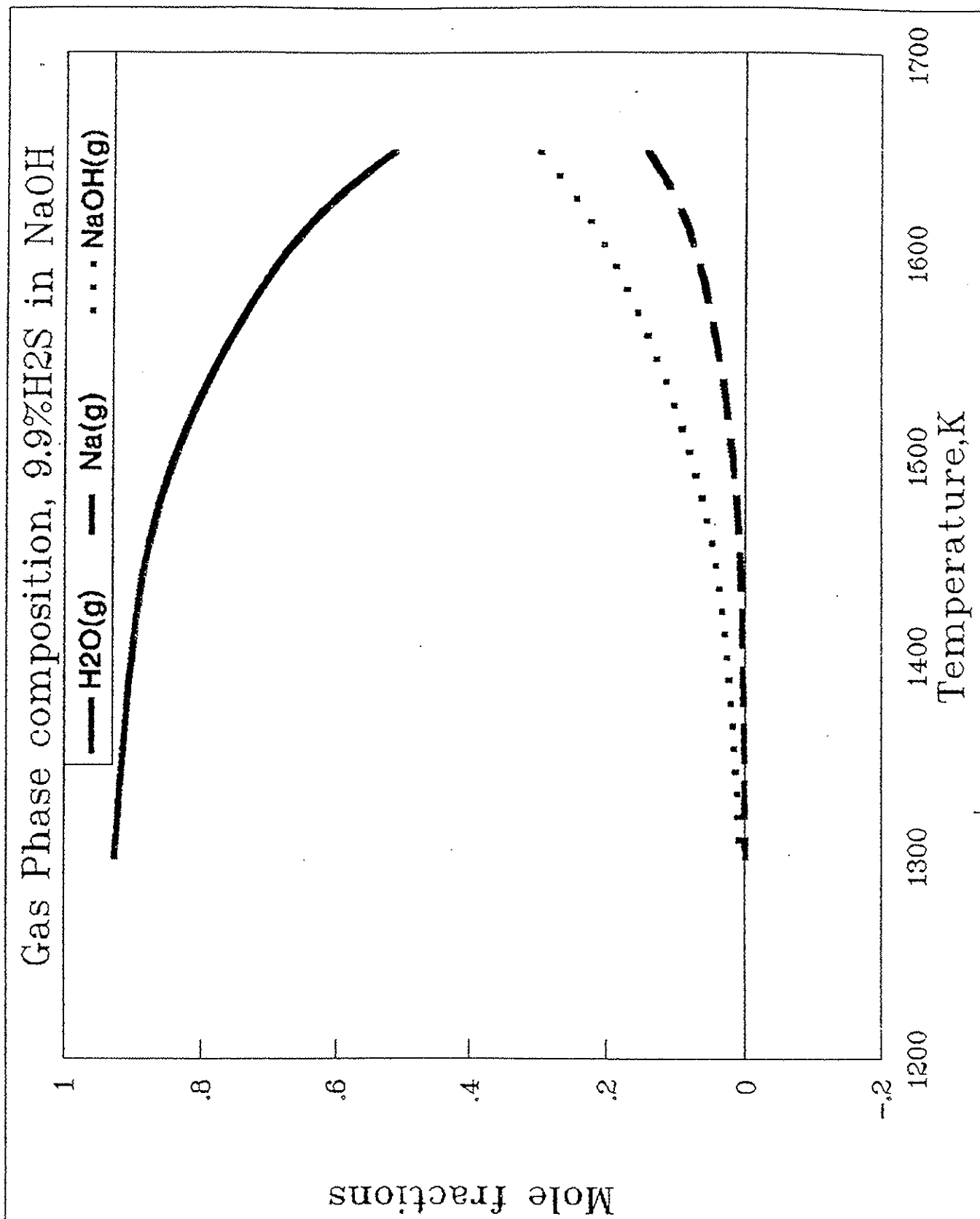
Fig. 3. Variation of the experimentally observed and the ideal conversions with temperature. The pressure used to calculate the ideal conversions is 0.033 atm, and since the feed rate was held constant at 0.1 mole/min, the experimental pressures actually varied from 0.026 to 0.037 atm.

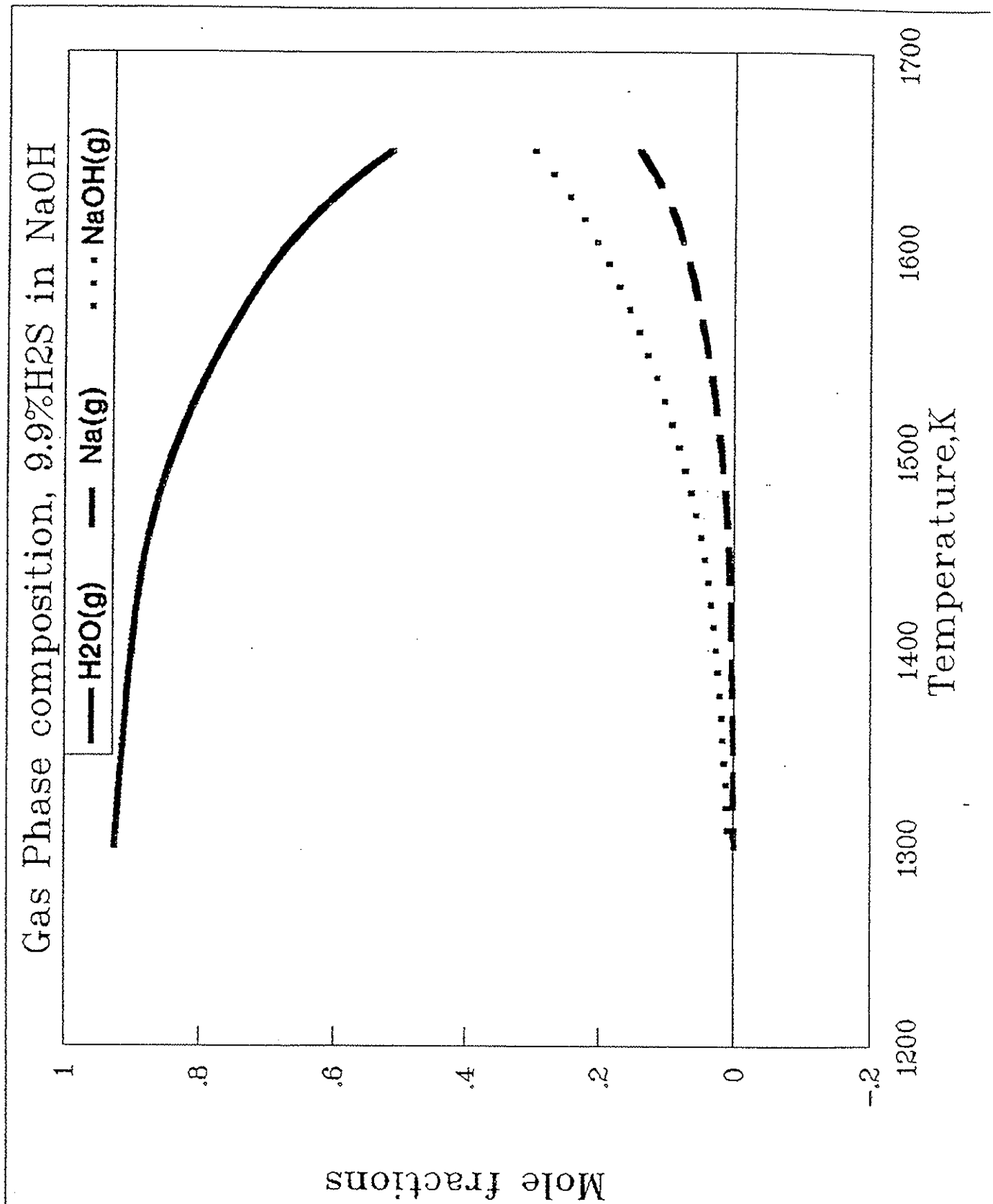
PAYBACK TIME FOR CAPITAL COST(a)
ZERO VALUE FOR H2S



(a) R.B. Diver and E.A. Fletcher, Energy 10, 831-842(1983).







A New Energy Global System: Combination of Solar Energy and Fossil Fuel Energy Using Metal Oxides

Yutaka Tamaura

Tokyo Institute of Technology

Research Center for Carbon Recycling and Utilization

2-12-1, Ookayama, Meguro-ku, Tokyo, Japan

Fossil fuel such as coal and methane can be combined with solar energy by the endothermic solar chemical process (Solar/Fossil energy mixing) (S/F-EM). By this process (S/F-EM process), solar energy is converted to chemical energy, which can be transported and stocked. Also, the sulfur in the fossil fuel will be removed using solar energy in the S/F-EM. This will reduce the air pollution load of sulfur causing acid rain. During the period of the shift from fossil fuel to solar energy, both fossil and solar energy should be used. The endothermic solar chemical reactions using metal oxides, which are attractive candidates and have been thermodynamically analyzed [1], are:

1. $\text{Coal} + \text{ZnO} = \text{CO (with small H}_2\text{)} + \text{Zn}$
2. $\text{Coal} + \text{Fe}_3\text{O}_4 = \text{CO (with small H}_2\text{)} + \text{Fe}$
3. $\text{CH}_4 + \text{ZnO} = \text{CO} + 2\text{H}_2 + \text{Zn}$
4. $\text{CH}_4 + \text{Fe}_3\text{O}_4 = 3\text{Fe} + 4\text{CO} + 8\text{H}_2$

In Eqs. 1 and 2, the reactants are solids. Eqs. 3 and 4 have been extensively studied [2, 3]. In this paper, we have studied the reaction rates of Eqs. 1 and 2. Based on the results for the reaction rates of Eqs. 1 to 4, a new energy global system, which can combine fossil fuels and solar energy, will be presented.

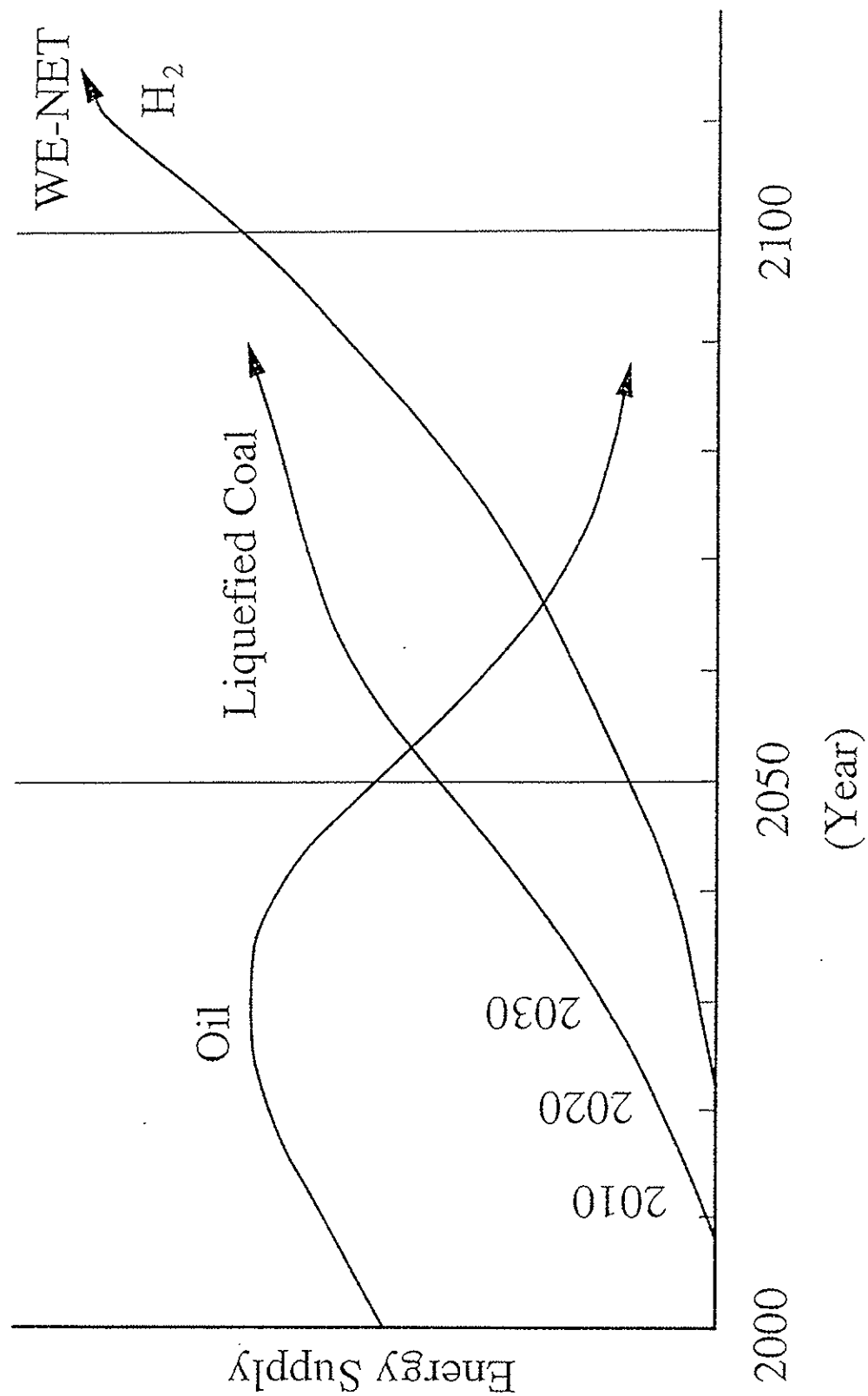
- [1] A. Steinfeld, *C&E'95 - Proc. Int. Symp. CO₂ Fixation and Efficient Utilization of Energy*, pp. 123-132, Tokyo, Nov. 29 - Dec. 1, 1993.
- [2] A. Steinfeld, P. Kuhn, J. Karni, *Energy - The International Journal* **18**, pp. 239-249, 1993.
- [3] A. Steinfeld, A. Frei, P. Kuhn, *Metallurgical and Materials Transactions* **26B**, pp. 509-515, 1995.

A New Energy Global System:

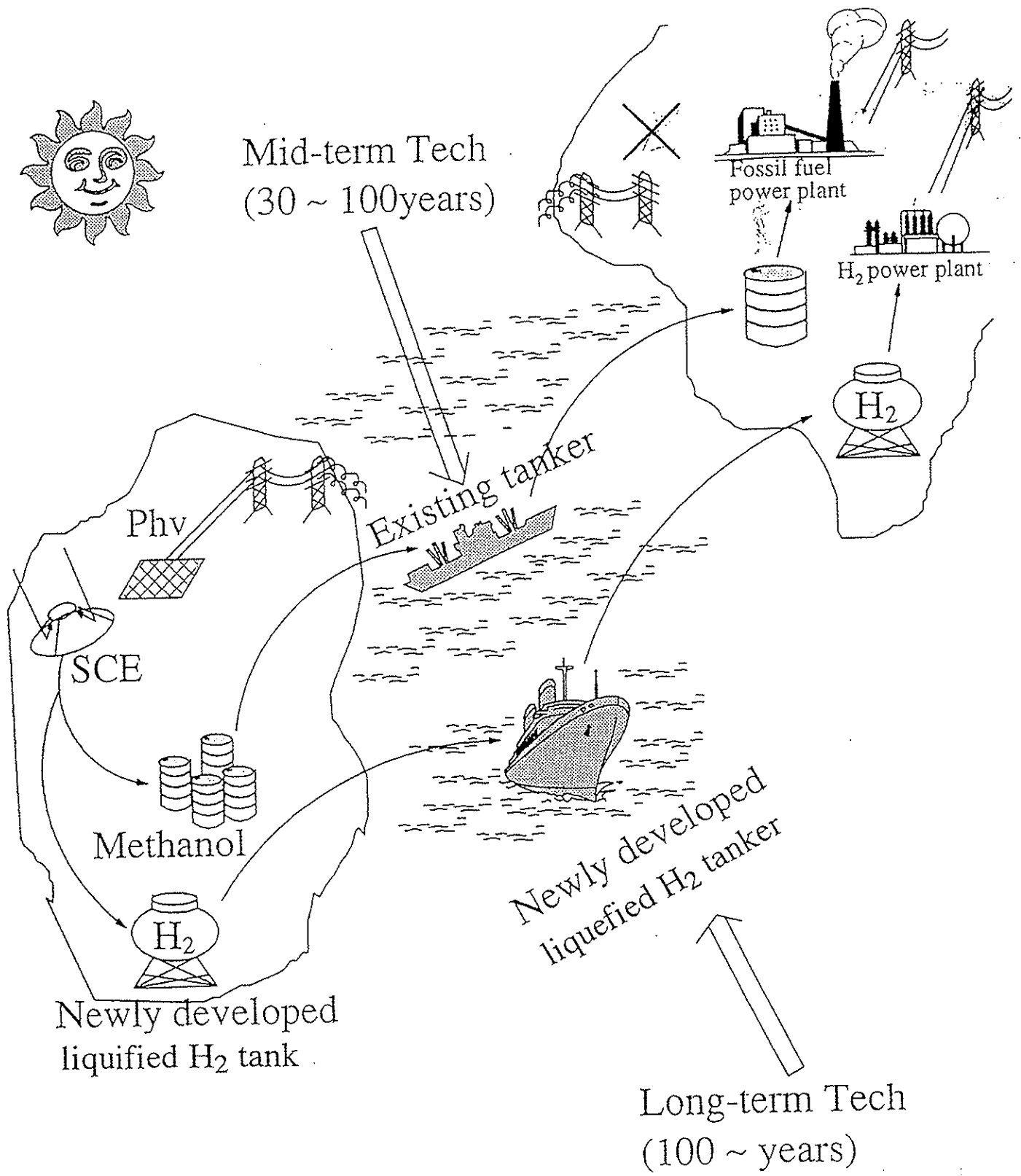
Combination of Solar Energy and Fossil Fuel Energy Using Metal Oxides

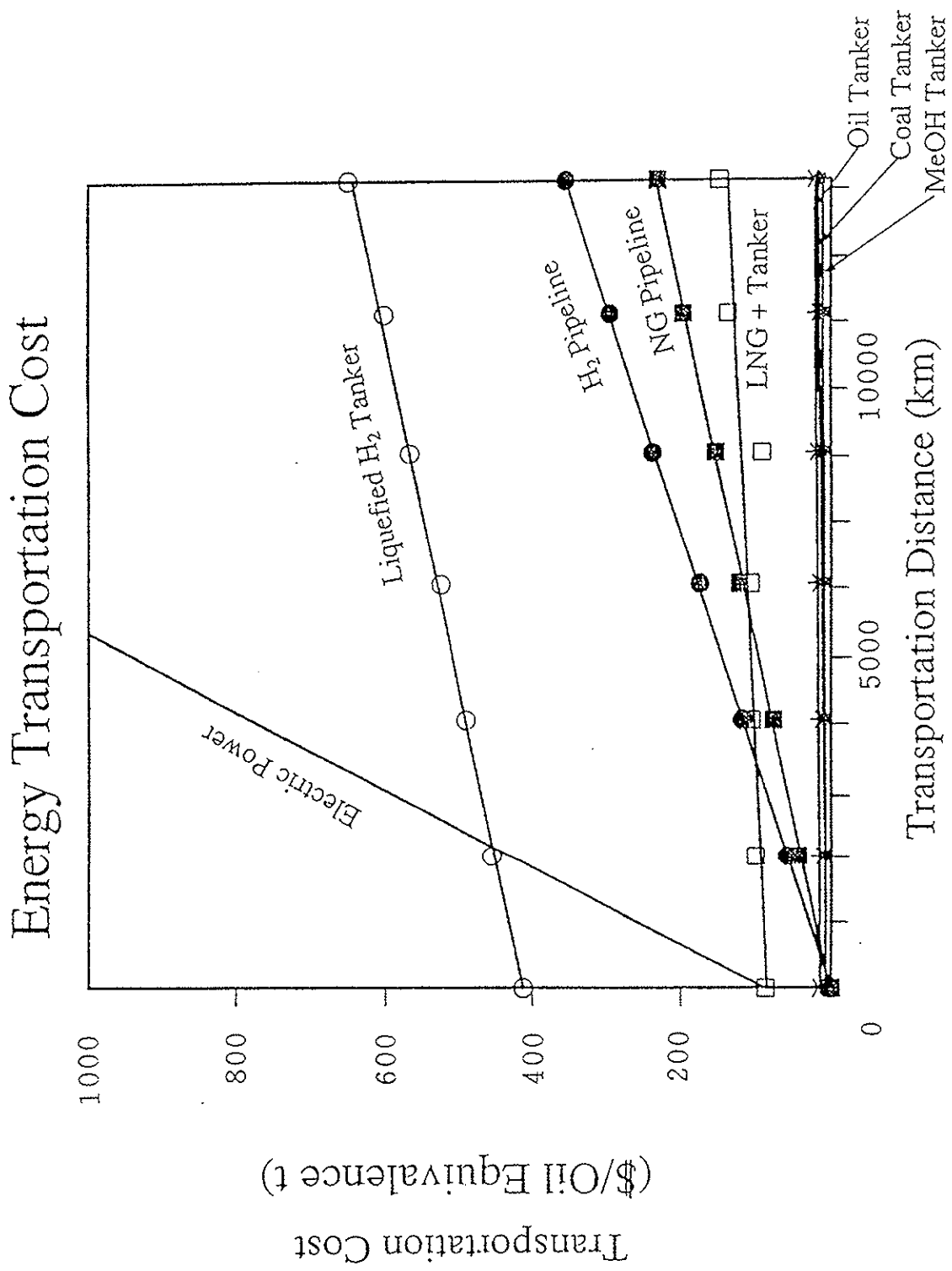
Yutaka Tamaura
Tokyo Institute of Technology
Research Center for Carbon Recycling and Utilization
2-12-1, Ookayama, Meguro-ku, Tokyo, Japan

Future Energy Supply Projection

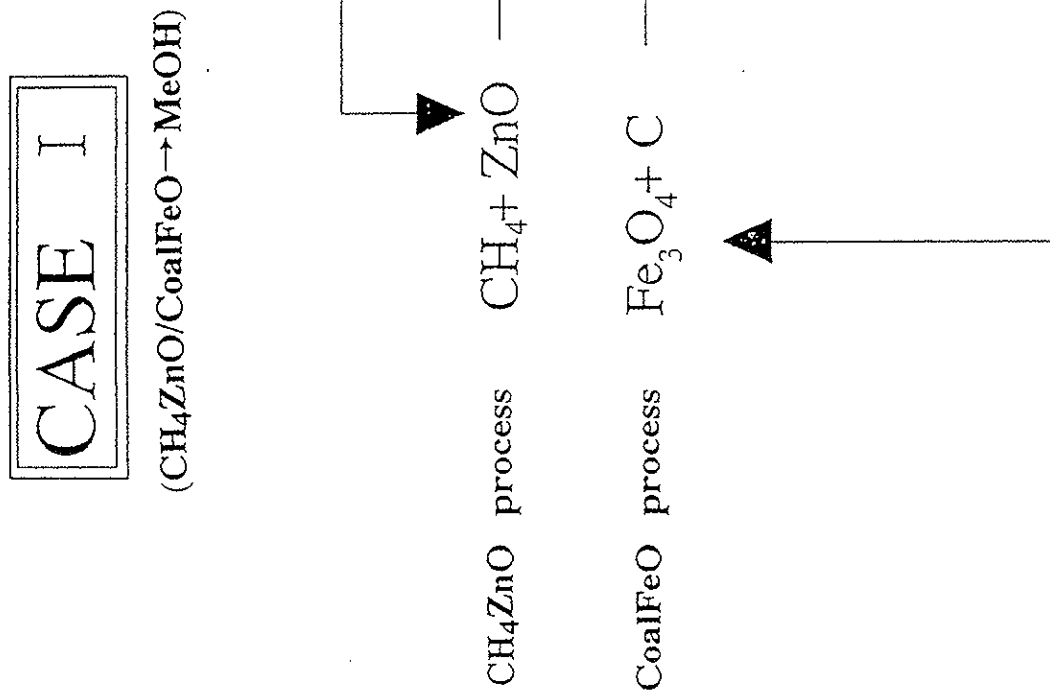


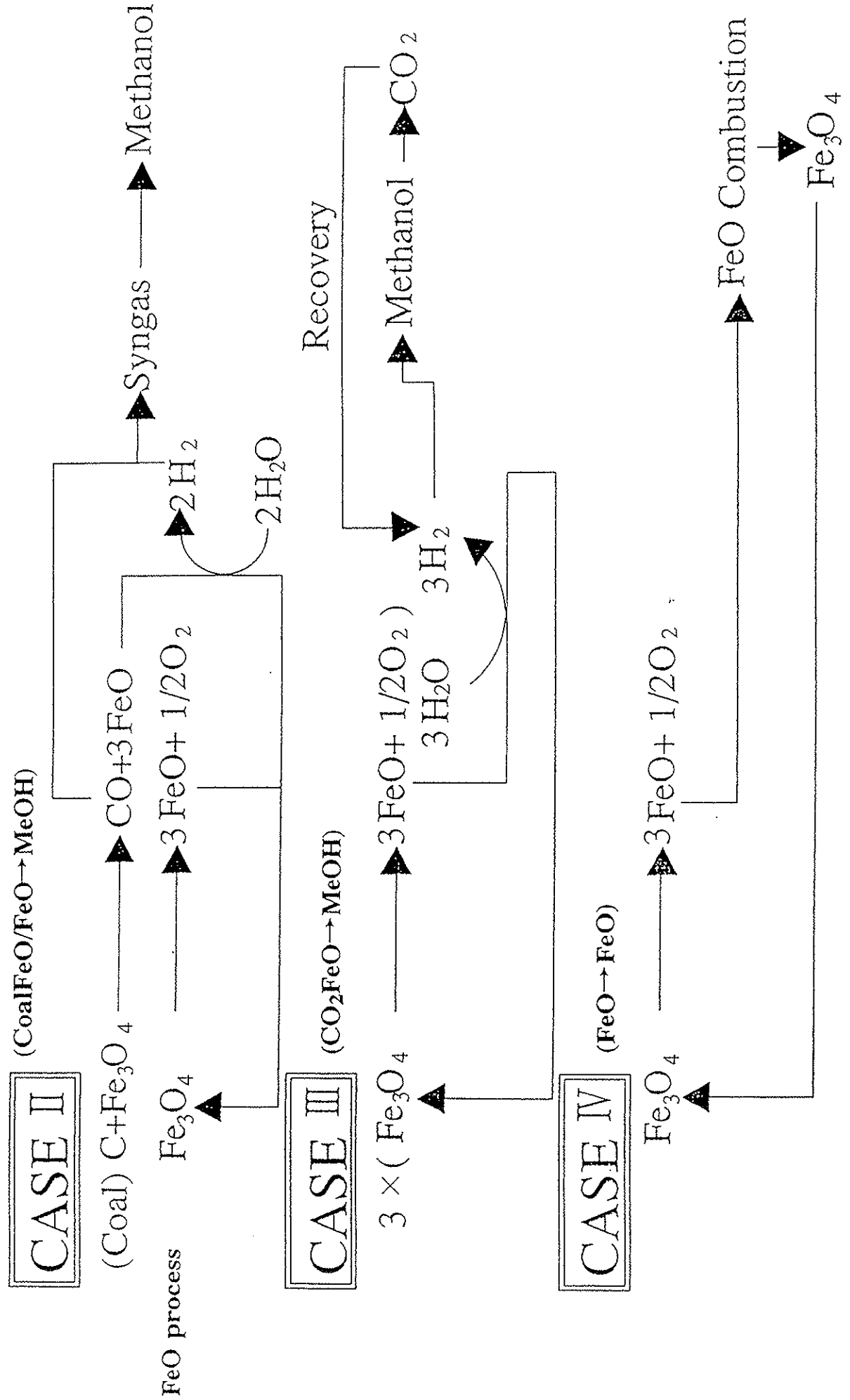
(A. Suzuki, Energy Review (Jpn), (3), 21-25(1993))

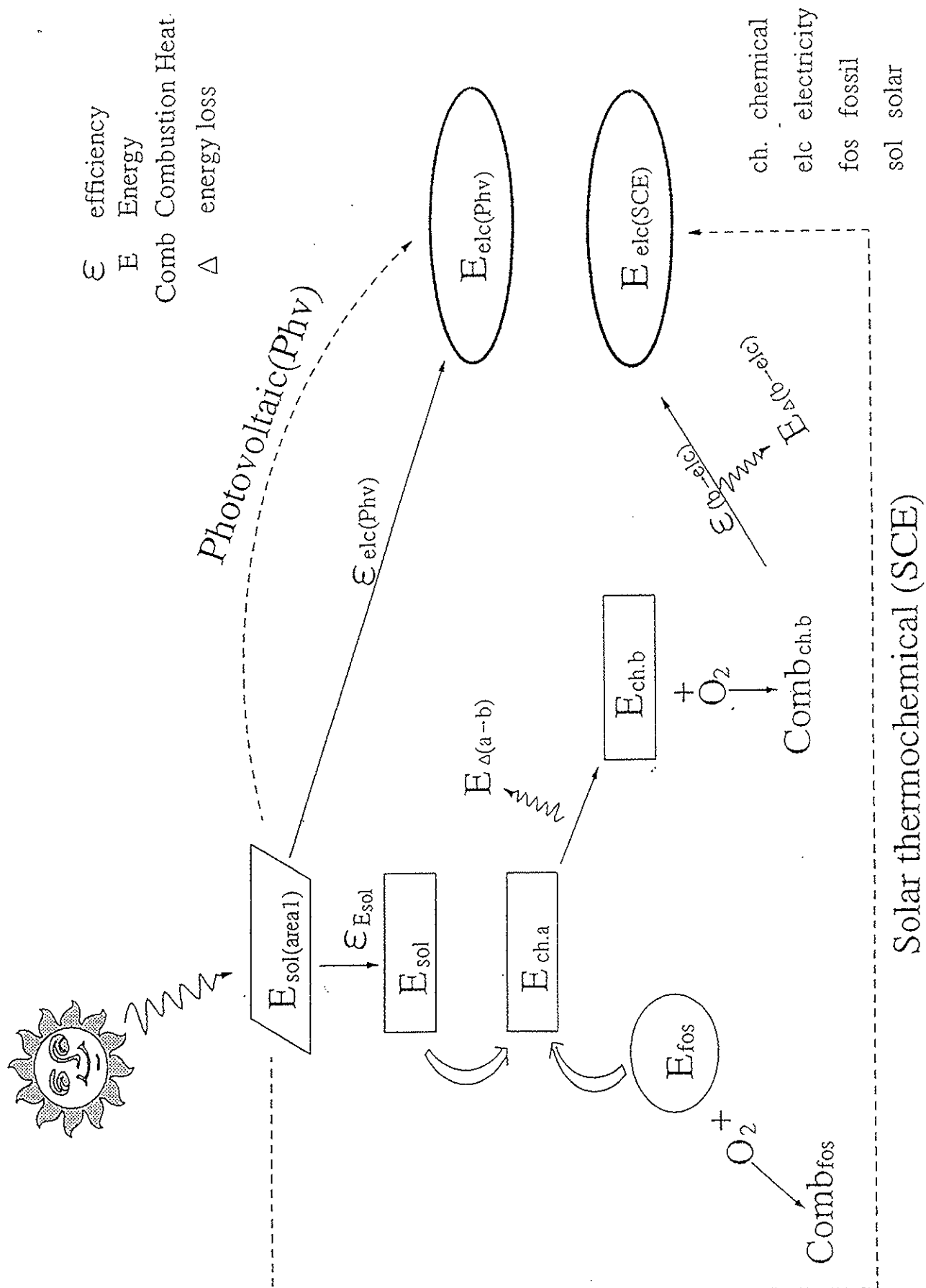


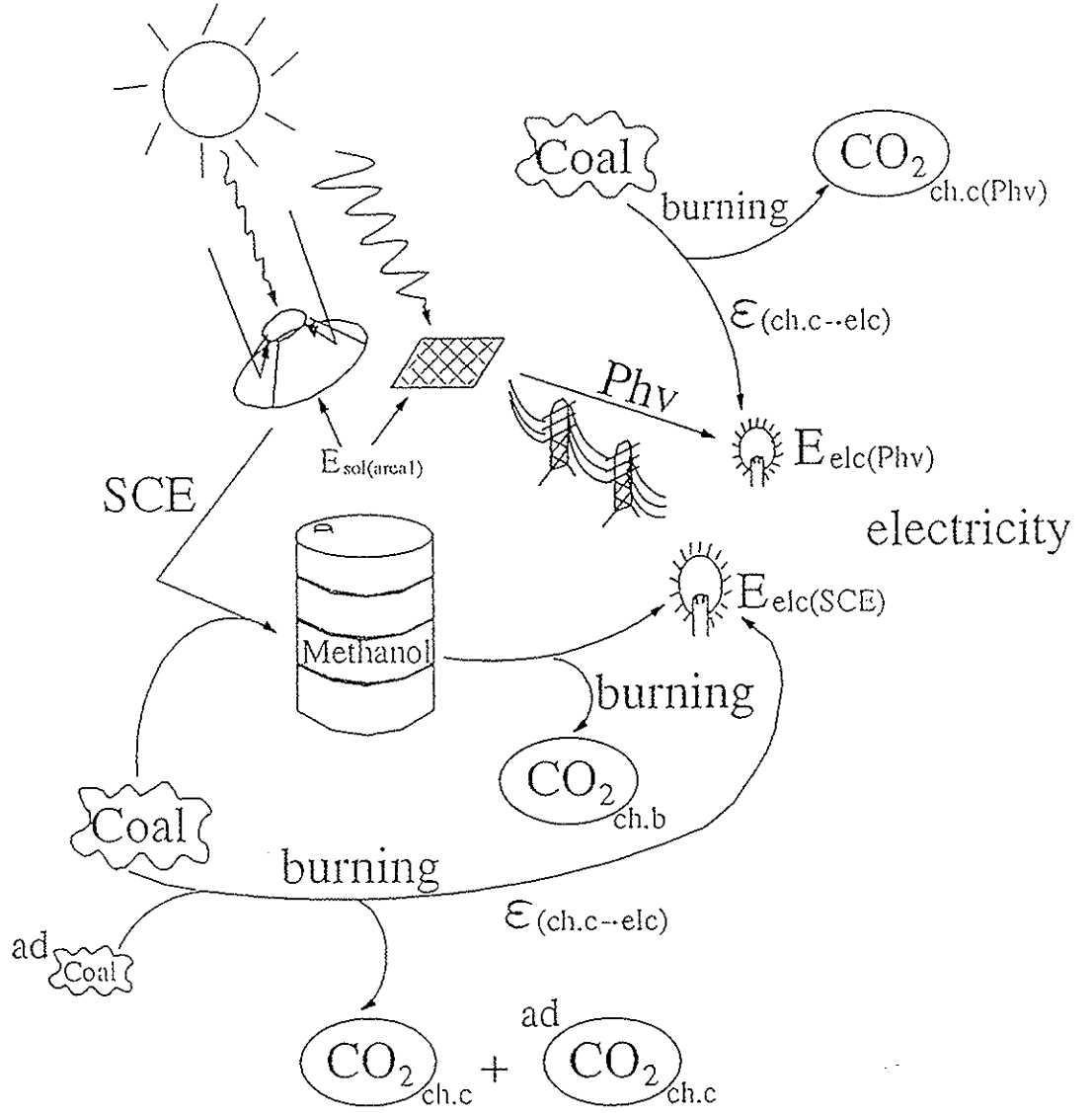


("Report on Oversea Clean Energy Transportation"
by Engineering Promotion Ass.(Jpn)(1991))









$$CO_{2_{ch.c(Phv)}} = \frac{E_{sol(area1)} \cdot \epsilon_{elc(Phv)}}{Comb_{ch.c}} \cdot \frac{1}{\epsilon_{(ch.c \rightarrow elc)}} \rightarrow E_{elc(Phv)}$$

$$ad\ CO_{2_{ch.c}} + CO_{2_{ch.b}} = E_{sol(area1)} \cdot \epsilon_{E_{sol}} \cdot \beta \cdot (1/Comb_{ch.c} - 1/Comb_{ch.b}) \rightarrow E_{elc(SCE)}$$

$$CO_2 + ad\ CO_2$$

$$Coal + ad(Coal) \rightarrow (Comb_{ch.c} + ad(Comb_{ch.c})) = Comb_{ch.b}$$

$$\boxed{\text{CO}_2 \text{ Reduction} / E_{\text{sol(area1)}}$$

$$\text{Phv} = \text{CO}_2_{\text{ch.c(Phv)}}$$

$$\text{SCE} = \text{CO}_2_{\text{ch.c}} + {}^{\text{ad}}\text{CO}_2_{\text{ch.c}} - \text{CO}_2_{\text{ch.b}}$$

$$\frac{\text{SCE}}{\text{Phv}} = \frac{\epsilon_{E_{\text{sol}}} \cdot \epsilon_{(\text{ch.c-elc})}}{\epsilon_{\text{elc(Phv)}}} \cdot \alpha \beta$$

$$\left(\alpha = \frac{\text{Comb}_{\text{ch.b}} - \text{Comb}_{\text{ch.c}}}{\text{Comb}_{\text{ch.b}}} \right)$$

$$= \frac{\epsilon_{E_{\text{sol}}} \cdot \epsilon_{(\text{ch.c-elc})}}{\epsilon_{\text{elc(Phv)}}} \cdot \alpha \beta$$

$$= \frac{(0.1 \sim 0.4)(0.3)}{(0.07 \sim 0.15)} \cdot \alpha \beta$$

$$= (0.20 \sim 1.71) \alpha \beta$$

Comparison of Solar Energy Utilization and CO₂ Reduction Efficiency in the Cases I ~ IV.

CASE	Solar energy absorbed (kJmol ⁻¹) (for 1 mol MeOH equivalent)	CO ₂ emission (molkJ ⁻¹) (reduction %)	Solar energy introduced ratio (α)	Solar energy contributed coefficient for chemical energy (β)	CO ₂ Reduction efficiency factor ($\alpha\beta$)	CO ₂ Reduction efficiency per $E_{sol(areal)}$ vs. Phv
I (CH ₄ ZnO/CoalFeO→MeOH)	256.3	0.00135 (21.6%)	0.115	2.64	0.304	0.061~0.52
(CH ₄ ZnO/CoalZnO→MeOH)	275.0	0.00129 (22.8%)	0.115	2.45	0.282	0.056~0.48
II (CoalFeO/FeO→MeOH)	511.2	0.000863 (34.0%)	0.417	1.32	0.550	0.11~0.94
III* (CO ₂ FeO→MeOH)	932.7	0 (100%)	1.00	0.724	-	0.14~1.2
IV (FeO→FeO)	675.6	0 (100%)	1.00	1.00	-	0.14~1.2
(FeO→H ₂)	869.8	0 (100%)	1.00	0.777	-	0.14~1.2
A (CoalFeO→MeOH)	300.5	0.00194 (23.7%)	0.126	2.25	0.284	0.057~0.49
Z (CH ₄ ZnO→MeOH,H ₂)	299.9	0.000954 (23.4%)	0.125	2.94	0.368	0.074~0.63

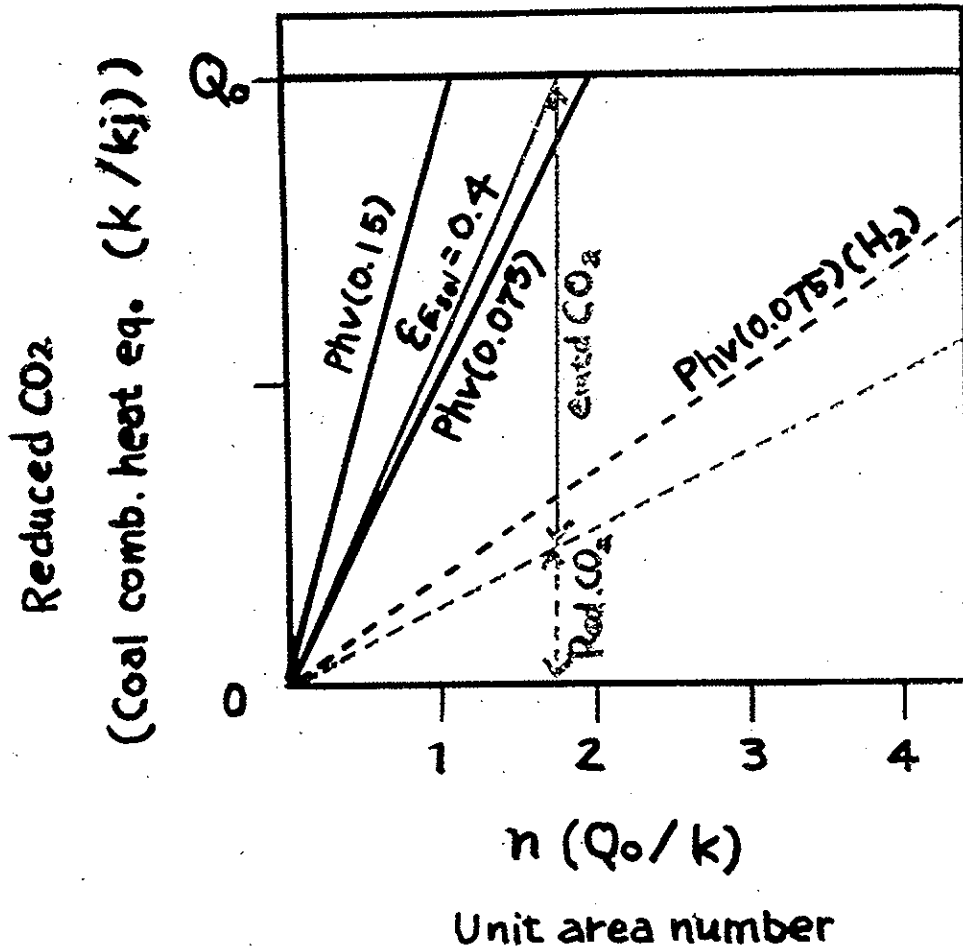
	Combustion heat(kJmol ⁻¹)
MeOH	675.6
C	393.5
CH ₄	802.7

* CO₂ Recovery energy penalty(0.7)

CO₂ reduction effectiveness

(Case I $\text{CH}_4\text{ZnO} / \text{CoalFeO} \rightarrow \text{MeOH}$)

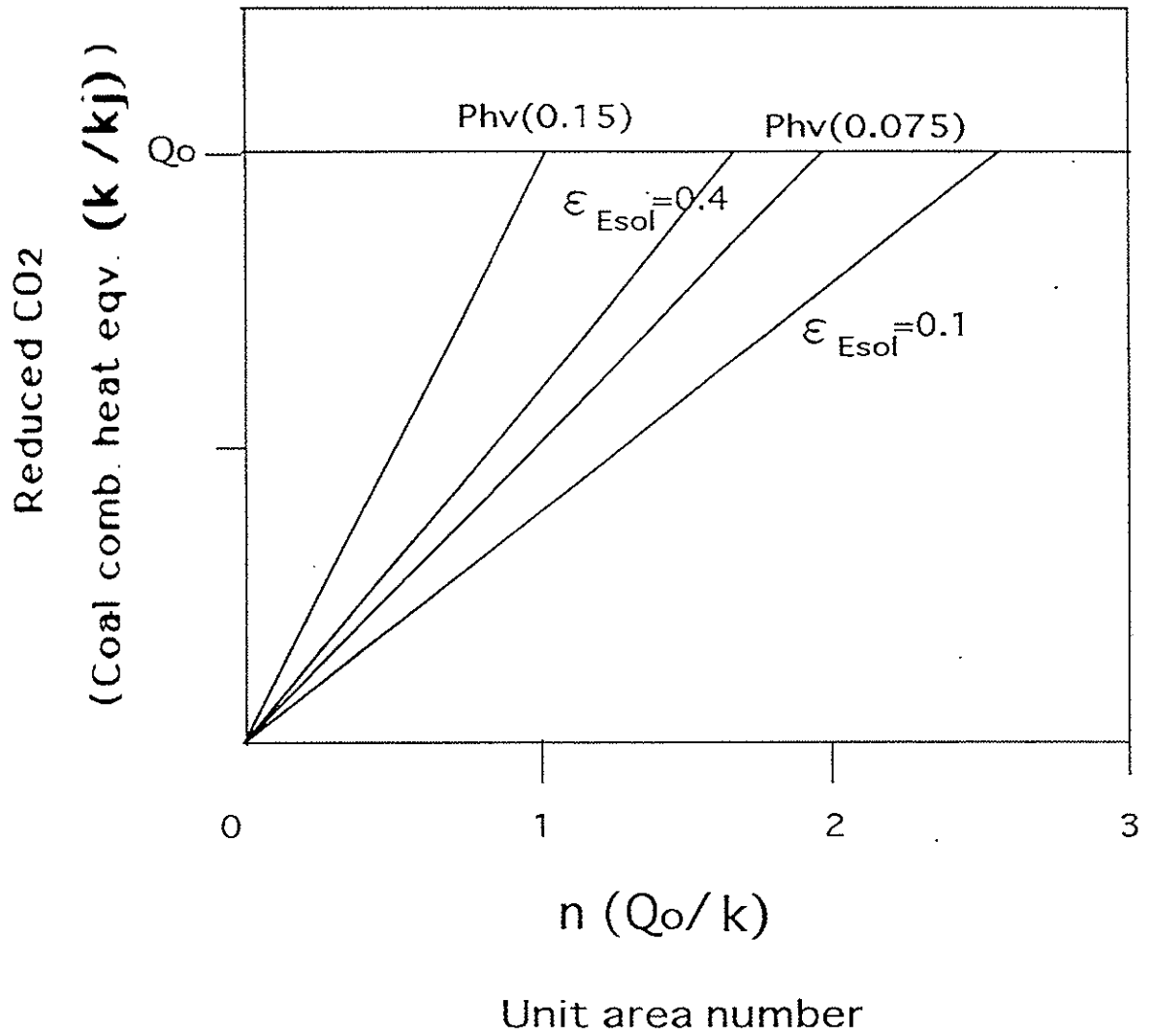
$$K = \frac{1}{2} \cdot E_{\text{Sol}(Q_{\text{req}1})} / \text{Comb}_{\text{ch,c}}$$

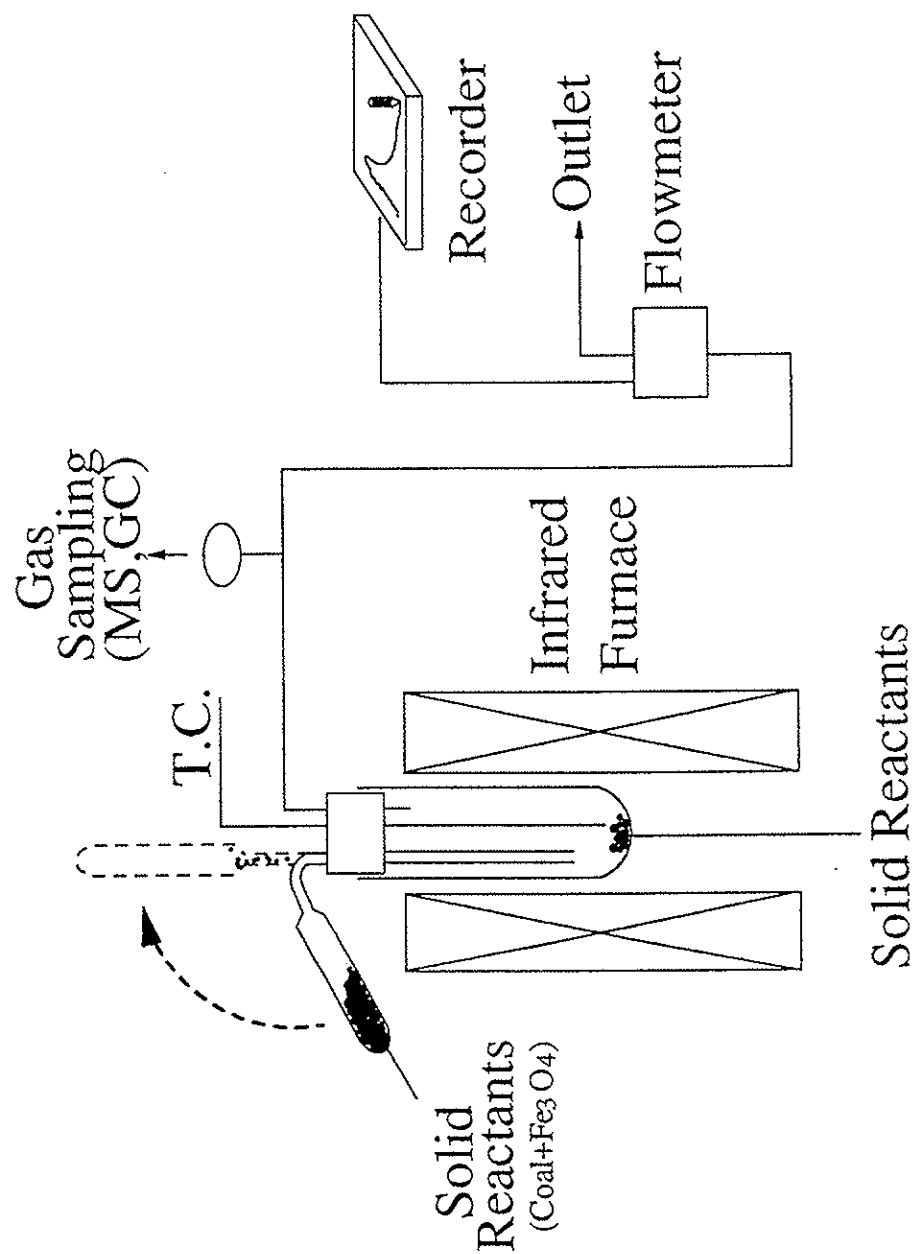


Comparison of CO₂ reduction effectiveness

(Case III CO₂FeO/FeO → MeOH)

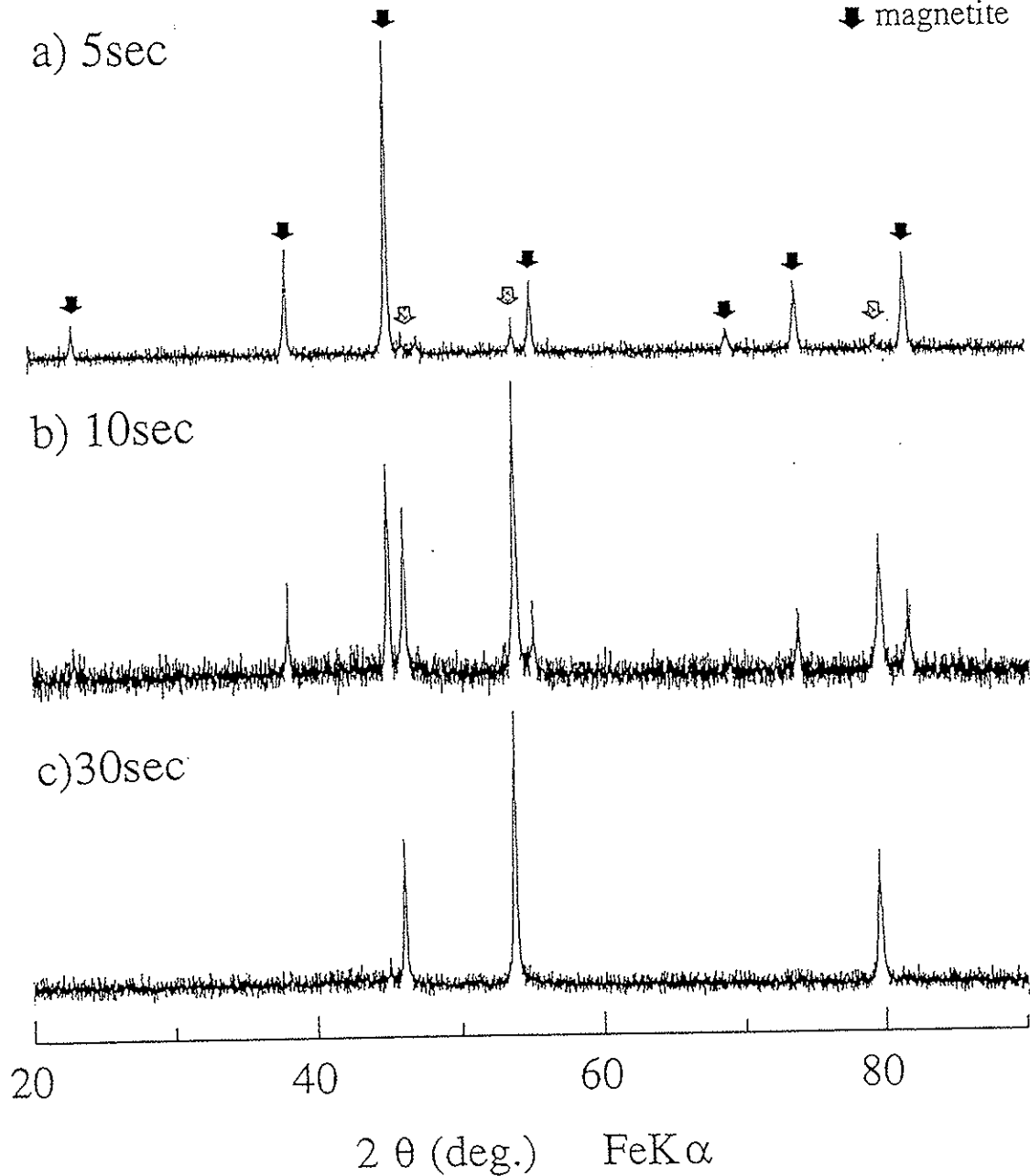
$$k = E_{\text{Esol(srea1)}}/2\text{Comb}_{\text{ch.c}}$$





Fe_3O_4 : 0.1184g
 Coal: 0.016g
 (Coal/ Fe_3O_4 = 1.2)

⊠ wustite
 ⊠ α -Fe
 ↓ magnetite



Phase change from $\text{Fe}_3\text{O}_4 \longrightarrow \text{FeO}$ at
 $\text{Fe}_3\text{O}_4/\text{FeO} = 1:1$ ($\text{Fe}_3\text{O}_4 + \text{C} \longrightarrow \text{FeO} + \text{CO}$). (1100°C)

External energy inputs required
to synthesize fuels from CO₂
can be used

to serve energy markets directly,
without incurring additional losses.

External energy → CO₂ → Fuel → Energy Market

"This is OK."

However,

△ How?, & What External Energy?

Reactivity of Solids - Basic Aspects for the Chemical Conversion of High-Temperature Solar Energy

H.R. Oswald
Institute for Inorganic Chemistry
University of Zürich
Winterthurerstr. 190
CH-8057 Zürich
Switzerland

The diversity of substances in their solid appearance is by far more abundant than in the other states of matter. Due to the rigid structure of most solids, their behaviour towards gaseous, or liquid, or solid reactants is fundamentally different from processes taking place in the homogeneous liquid or gaseous states of aggregation. In the given context of high temperature solar energy conversion our interest is centered on the thermal reactivity of metal oxides. Apart from the obvious condition that a process aiming in the storage of energy has to be endothermic, the respective thermodynamics are not emphasized. Rather the kinetics and mechanistic, based on transport properties, exert a crucial influence on the course of heterogeneous solid state reactions. Investigations on the reactivity of solids as a function of the external parameters temperature, pressure, atmosphere, perhaps irradiation, require the use of well defined samples. A solid is, however, by far not sufficiently characterized solely by its chemical composition and crystal structure. In addition, further properties constituting the 'individuality of solids' such as size and shape of particles, crystallographic faces making up the surface, texture, domain structure, specific kinds of lattice defects as e.g. vacancies in nonstoichiometric oxide phases, optical properties, etc. are decisive for the thermochemical reactivity. Therefore a consistent description of the chemical behaviour of solids requires manifold complementary techniques of investigation.

In particular, these general considerations will get illustrated by extracts from a recent Ph.D. thesis [1] in the framework of a collaboration between the Solar Chemistry Group at the PSI and our Institute. It deals with a two step process cycle: the solar thermal reduction of magnetite resp. iron

manganese spinels at temperatures above 2000 K, followed by the oxidation of the resulting $\text{Fe}_{(1-y)}\text{O}$, wustite resp. manganowustite by water vapour in a low temperature region of 600 - 700 K under formation of molecular hydrogen. On the high temperature side it is shown that the insertion of bivalent manganese or cobalt into the Fe_3O_4 -lattice leads to a significant lowering of the thermal reduction temperature. Nevertheless reaction times in the order of seconds have to be achieved. The experiments on the reoxidation of the metal oxide [2] proved that the efficiency to split water remains. Detailed kinetic experiments about the reactivity of ternary metal oxide phases under defined water vapour pressure were undertaken in a fixed bed reactor and quantitatively followed by gas analytical techniques. They resulted furthermore in defining an optimal composition $(\text{Fe}_{0.9}\text{Mn}_{0.1})_{0.97}\text{O}$ for the envisaged purpose.

- [1] K. Ehrensberger, *Zweistufiger Metalloxidzyklus zur chemischen Speicherung von Sonnenenergie: Kinetische Untersuchungen thermochemischer Redox-Reaktionen an binären und ternären Eisenoxidphasen mit Kochsalz- oder Spinellstruktur*; Diss. Univ. Zürich, 1995.
- [2] K. Ehrensberger, A. Frei, P. Kuhn, H.R. Oswald, P. Hug; *Solid State Ionics* 78 (1995) 151.

Reactivity of Solids — Basic Aspects for the Chemical Conversion of High-Temperature Solar Energy

H.R. Oswald

Institute for Inorganic Chemistry, University,
Winterthurerstrasse 190, CH-8057 Zürich / Switzerland

Introducing myself I have to say that I am no specialist for Solar Energy Conversion or related topics, but just an Inorganic Chemist with some experience about the Solid State. In addition to the generation of new phases and determination of their structure and physical properties, this field also encloses the investigation of the **Reactivity of Solids**. This term comprises the behaviour of a solid substance when confronted with chemical partners in another solid, or a liquid, or a gaseous phase, and also the influence of heat. The main goal of such work is to correlate the macroscopically observable processes with those occurring on a microscopical, even atomic level.

[Folie 1]

This sounds quite simple — but, as we all know, due to the rigid structure of most solids, their reactions proceed fundamentally different from those in the homogeneous liquid or gaseous states of aggregation.

The contacts which have developed during the last few years between the Solar Chemistry Group at the Paul Scherrer Institute and the Solid State Division of the Inorganic Chemistry at the Zurich University are, at least to my opinion, of mutual interest. Our tradition in dealing with metal oxide systems meets indeed well with the activities at the PSI in high temperature solar energy conversion by means of oxides. Besides the demand that a process aiming at the storage of energy must be endothermic, thermodynamic aspects are not in the center of our interest. There are rather the kinetics and mechanistics which — based on transport properties — exert a crucial influence on the course of heterogeneous solid state reactions. If you can forgive me the simplicity of this comparison, I may mention that the negative value of the Gibbs Free Enthalpy (per mole oxygen) for the oxidation of aluminum is about four times as big as the one of copper — the velocity of aluminum oxidation at 500 to 600°C is, however, by orders of magnitude **slower** than the one of copper!

Investigations on the reactivity of solids as a function of the external parameters temperature, atmosphere, pressure, perhaps irradiation require the use of well defined samples. A given solid is, however, not sufficiently characterized by merely knowing its chemical formula and crystal structure.

[Folie 2]

Instead, there are numerous further properties constituting the 'individuality' of solids and strongly influencing their behaviour. Therefore, a consistent description requires the use of manyfold complementary techniques of investigation (analytical, structural, morphological, etc.).

Extracts from the recent Ph.D. thesis by Köbi Ehrensberger will serve now as a more concrete information about the specific systems which are dealt with. They root in a two step process cycle first proposed by Nakamura in 1977: the solar thermal reduction of magnetite resp. ternary iron metal spinels at temperatures above 2000 K, followed by the oxidation of the resulting $\text{Fe}_{(1-y)}\text{O}$, wustite resp. manganowustite by water vapour in a low temperature region of 600 - 700 K under formation of molecular hydrogen.

[Folie 3]

The motivation to use ternary oxides is to influence the solid state chemical properties of the involved spinels resp. their thermal reduction products.

On the high temperature side, thermodynamic calculations reveal that ΔG_R for the thermal reduction of the spinel phase Mn_3O_4 to MnO equals zero at about 500 K lower temperature than for magnetite.

[Folie 4]

Such an effect is desirable for technical reasons but, unfortunately, the rock salt type MnO is no more able to split water as FeO (resp. Fe_{1-y}O) well does.

As high temperature investigations in the powder clouds finally striven for are not very easy for us, two types of **model** experiments on pressed pills were performed:

- in the laboratory with a HT furnace
- on the solar furnace.

As non-iron metal M, mainly Mn was chosen, but also Co, Ca, Mg, Zn looked at. The laboratory experiments with 10 s irradiation prove that introduction of M definitely reduces the reduction temperature.

[Folie 5]

For the solar furnace tests, a device named "SAROCOI" was constructed by Köbi Ehrensberger.

[Folie 6]

It allows an exact monitoring of the gas atmosphere resp. oxygen production by mass spectrometry, control of the reaction time at a resolution of 1/10 s, both at known flux density distribution. It could for instance be proved that with Mn-dotation a significantly shorter reaction time is sufficient to achieve the thermal decomposition.

[Folie 7]

As the product analysis by X-ray diffraction demonstrates, the (200) reflection of the rock salt phase appears after 1 s under presence of Mn, but only after 1.5 - 2 s using pure magnetite.

A factor which is not yet sufficiently known is the radiation absorption of the solid and its temperature dependence (set equal for the compared materials in first approximation). Nevertheless, the results indicate that it will be possible to achieve fast enough reduction of the about 10 μm particles in a powder cloud. In parallel to our laboratory work there were permanently and still are also near-application experiments in powder cloud flow through reactors by Peter Kuhn and coworkers, to whom I acknowledge these transparencies.

[Folien 8, 9]

In our experiments, only little dependence from the kind of the atmosphere (argon or air) was observed, and the product exhibits no segregation into Mn-rich or poorer phases. An undesired side effect is the oxidation of magnetite to hematite, as observed by the appearance of its (113) reflection. Evidently, this oxidation is lowered by shorter time of reduction. Certainly, there is still much work needed on the HT-side.

Now to the low temperature part of the circle. It regards thus the re-oxidation of the monoxide with water vapour at moderate temperature, i.e. the "water splitting" under formation of molecular hydrogen. This topic is contained in very detail in the said thesis by Mr. K. Ehrensberger. He synthesized manganowustites with varied manganese content by preparative solid state chemical standard procedures, under inert atmosphere, followed by adequate quenching, as below 570°C, the pure iron oxide is metastable and tends to disproportionate into metallic iron and magnetite. In general, the manganese content stabilizes the rock salt phase.

With these products, kinetic experiments were performed in a fixed bed reactor under defined water vapour pressure and mass spectrometric detection of the hydrogen formed.

[Folie 10]

Typical results for the hydrogen production as function of time and the temperature, here for the pure iron oxide, look as follows:

[Folie 11]

The dependence on the manganese content, at 873 K and for a water partial pressure near 0.1 bar is shown on the next transparency.

[Folie 12]

Without manganese, the hydrogen evolution is fastest. It remains reasonably fast with 10 % manganese, but gets slower and slower with increasing Mn-content. Printing the conversion α resp. $(1-\alpha)$ versus time, as usual in solid state kinetics, illustrates an analogous behaviour.

[Folie 13]

Particularly interesting is to consider the average reaction velocity versus the manganese content.

[Folie 14]

The black squares represent the experimental results, whereas the green crosses refer to the diffusion coefficients of iron in iron-manganese-spinel phases which are fortunately available from recent work in literature. The excellent fit leads to the conclusion that the diffusion of iron in the (product) spinel represents the reaction rate determining step.

It is well necessary to say something about the **phase analysis**. In order to follow the manganese content in the initial and product phases, eight samples of the same initial composition were oxidized, but quenched after different time of reaction (slide 1), and subjected to a phase analysis by X-ray diffractometry. The results are as follows:

[Folie 15]

After 5 min one finds a rock salt phase with slightly lowered manganese content and a product spinel phase relatively poor in manganese. As the reaction proceeds, two rock salt phases are found — the already mentioned one and another with much higher manganese percentage. This is clearly a segregation effect. After still longer time (25 min oxidation), the manganese percentage of the spinel phase is continuously arising, and there is again only one, manganese rich rock salt phase. The hydrogen production slows much down in this period. We end up with a homogeneous manganese-iron-spinel corresponding to the Fe : Mn ratio of the initial sample. Evidently, there is taking place a solid-solid reaction among a Mn-rich rocksalt and a Fe-rich spinel phase, under uptake of oxygen from water. These observations have been supplemented by X-ray photoelectron spectroscopy and by direct observation using analytical transmission electron microscopy. The comparison of the Mn-distribution (left on slide 2) and the Fe-distribution at time zero prove the homogeneity of the rock salt initial phase. After a reaction time of 15 min, however, manganese-rich islands (left on slide 3) in the order of 1 μm are found, besides iron-rich domains (right). The percentages are, although at considerable limits of error, in good agreement with the mentioned results from the lattice constants by X-ray diffractometry. The main result is that at sufficient temperature, the product spinel is homogeneous at the end of oxidation.

Finally I may mention an interesting side effect of the manganese dotation, namely — within given limits — an increase of the amount of hydrogen formed. One would believe at first sight that replacement of Fe by Mn must provoke a decrease of hydrogen, as manganese remains bivalent till the end of the oxidation process. **But:** introduction of Mn also influences the non-stoichiometry coefficient y of the rock salt phase, which amounts up to 10 % for the pure, manganese-free wustite and falls to 3 % or less upon replacement of only 10 % of the iron by manganese. This effect overcompensates the effect of the loss of redox-active iron and leads to the calculated and experimentally proved effect that the amount of hydrogen form reaches a maximum at the composition $(\text{Fe}_{0.9}\text{Mn}_{0.1})_{0.97}\text{O}$ of the rock salt phase!

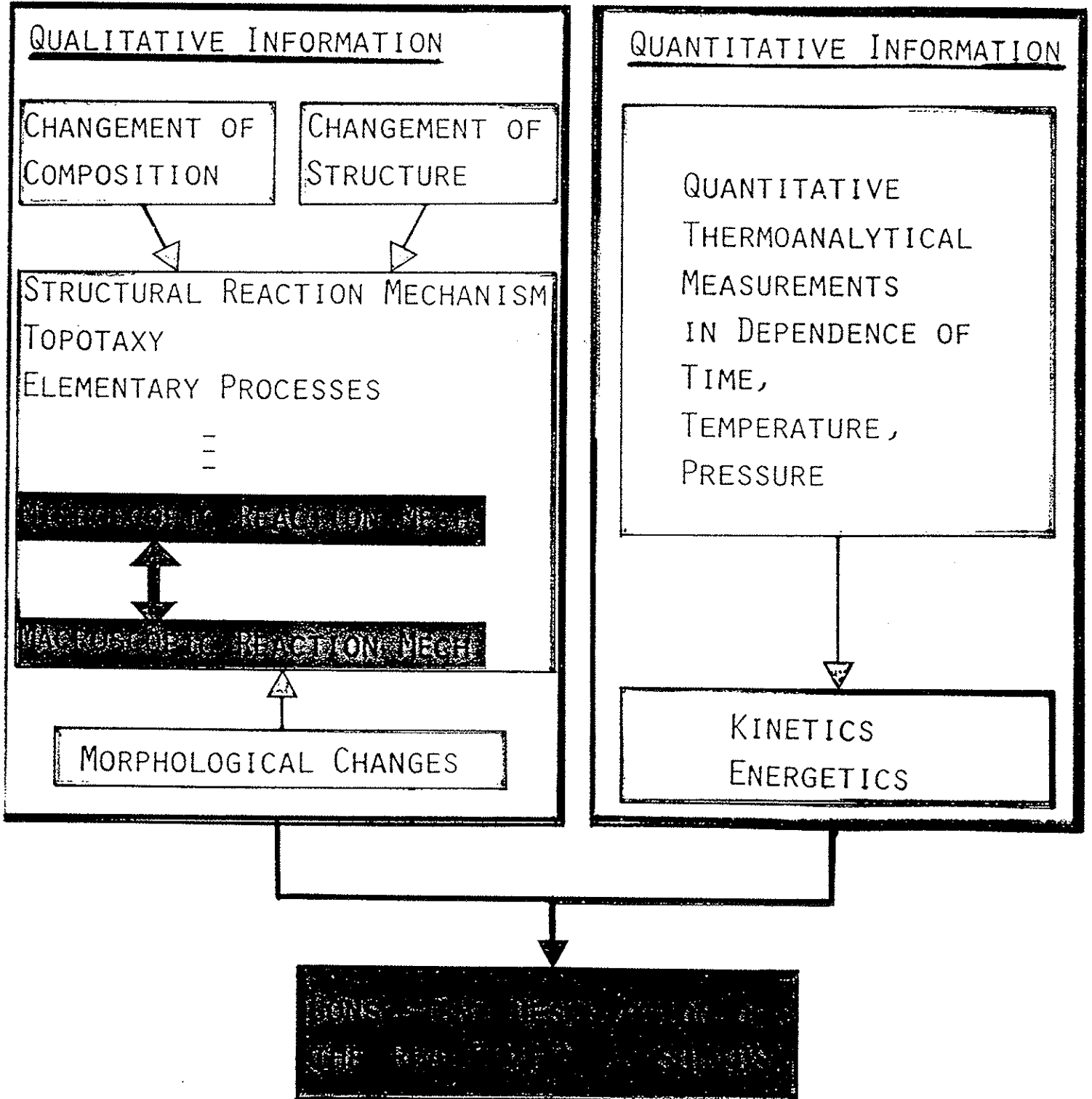
[Folie 16]

Many points could still be mentioned, and even much more remains to be done. But in favour of some discussion, I shall better stop now with just two statements:

- I hope having been able to demonstrate to you that there is a lot of interesting solid state chemistry in the given and other similar systems, and
 - The expression of my heartiest thanks to Dr. Paul Kesselring for his continuous support, to Dr. Peter Kuhn as leader of the Solar Chemistry group, and to Dr. Köbi Ehrensberger and his successor Peter Nüesch who really did the job. Finally I have to acknowledge also the Swiss National Foundation for financial means, and to thank you for your kind attendance.
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THEORY OF REACTION KINETICS

THEORY OF REACTION KINETICS



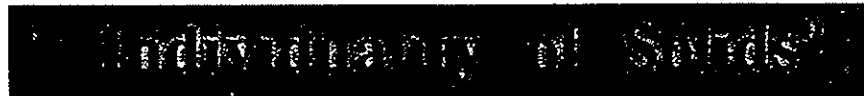


Statements:

A solid is **not** fully characterized by its chemical composition (formula) and crystal structure

Solids are reacting as "individuals"

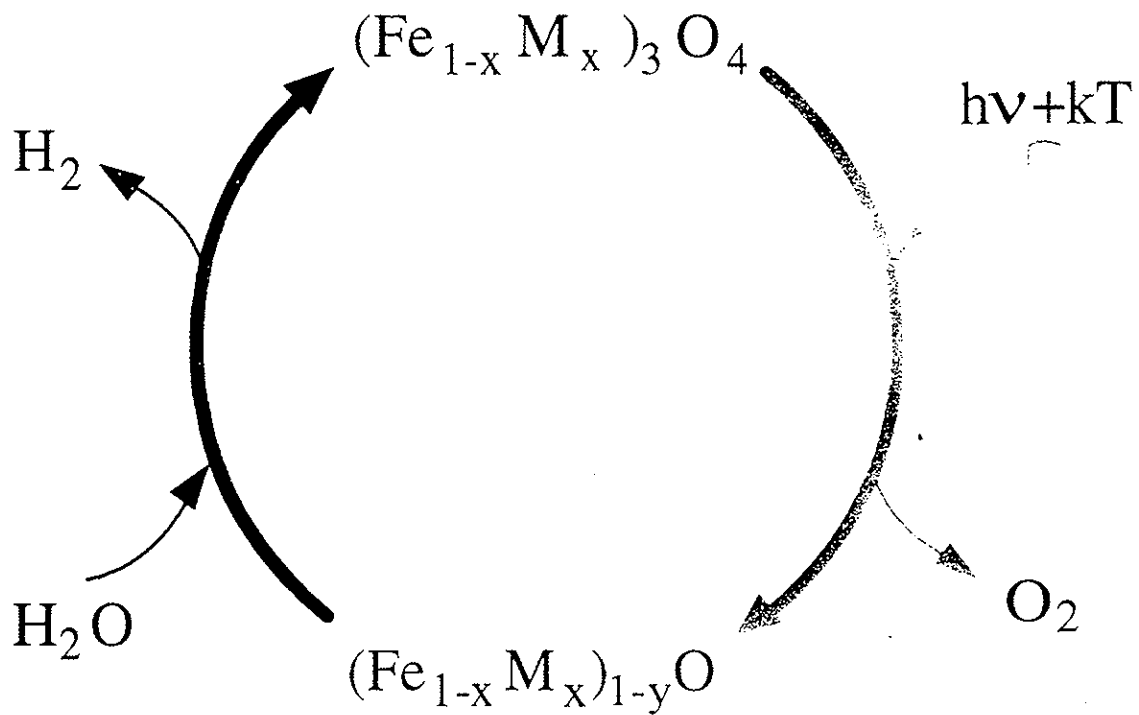
Examples of properties which make up the



"Individuality of Solids"

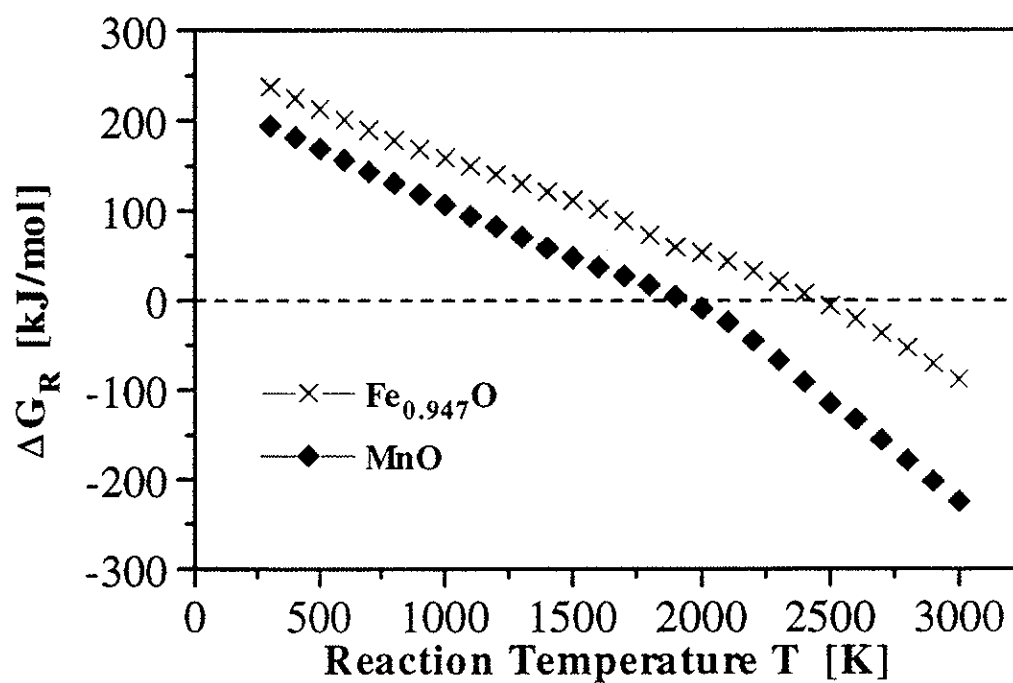
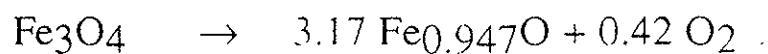
- particle size resp. distribution function
- shape of particles (primary / secondary?)
- crystallographic faces making up the surface
- type and extent of orientation of crystallites (texture)
- domain structure (in multiphase systems)
- lattice defects (ordered / statistic)
(—> non stoichiometry)
- optical properties
- etc.

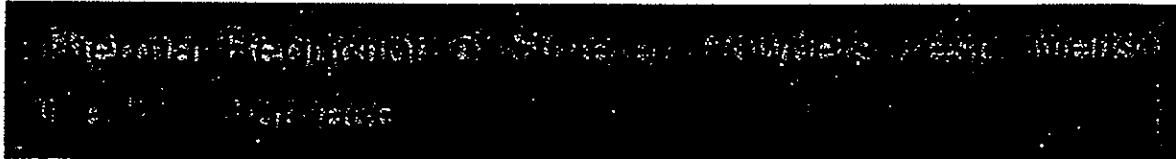
Metal Oxide Cycle with Ternary Oxides



$\text{M} = \text{Ca}, \text{Co}, \text{Mg}, \text{Mn}, \text{Zn}, \text{Li}, \dots$

Thermal Reduction

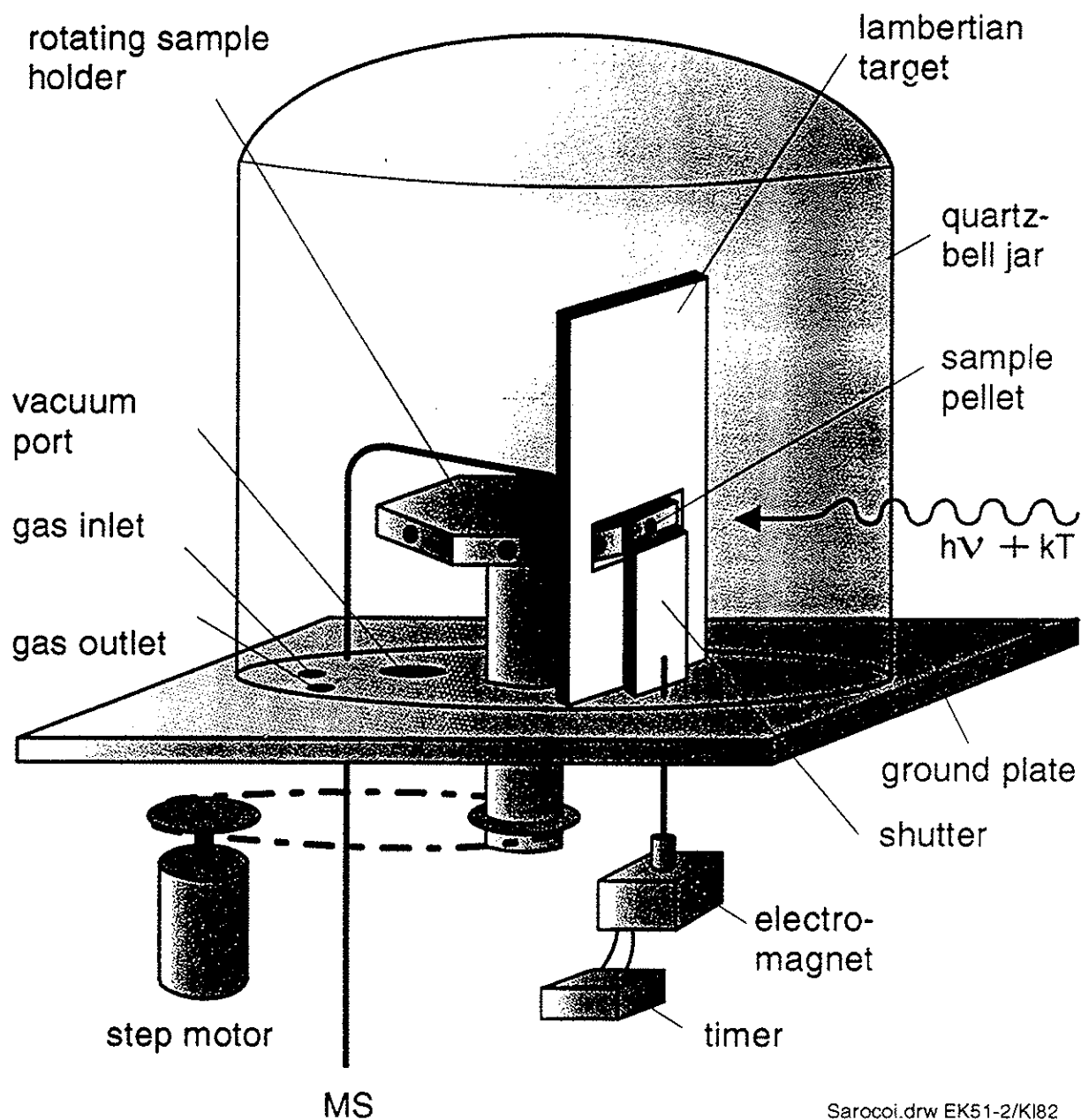




starting oxide	dotation	thermal reduction temperature [K] for $\alpha=0.5$ *)
Fe_3O_4		2100
$(\text{Mn}_{0.3}\text{Fe}_{0.7})\text{Fe}_2\text{O}_4$	10 % Mn	2050
$(\text{Mn}_{0.9}\text{Fe}_{0.1})\text{Fe}_2\text{O}_4$	30 % Mn	2030
$(\text{Co}_{0.3}\text{Fe}_{0.7})\text{Fe}_2\text{O}_4$	10 % Co	2035

*) α = degree of conversion

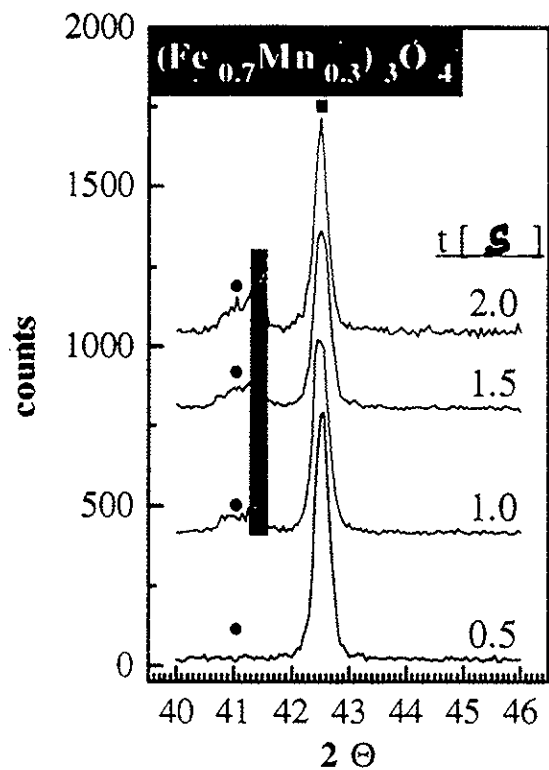
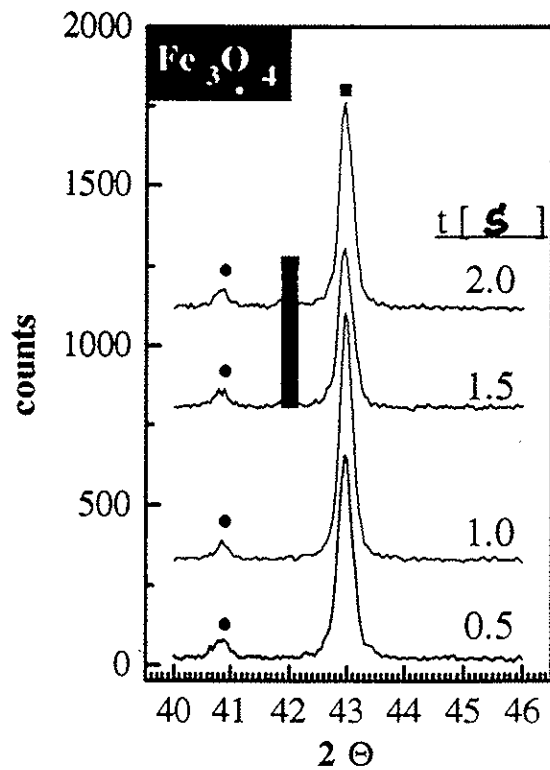
Diploma Thesis
P. Nüesch (1995)

SAROCOI**(Sample Rotor for Controlled Irradiation)**

Sarocoi.drw EK51-2/KI82

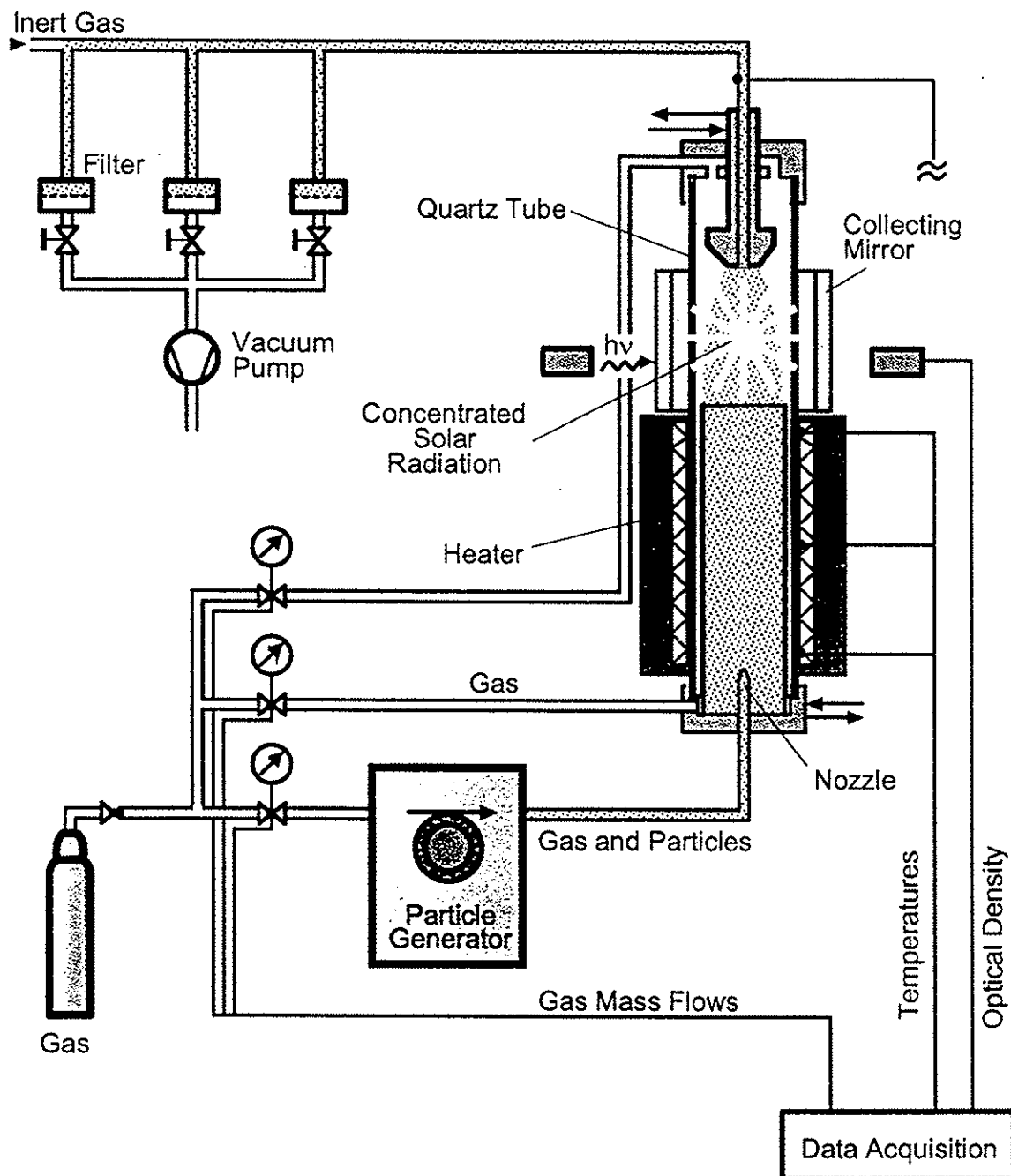
Comparison of the Required Illumination Time

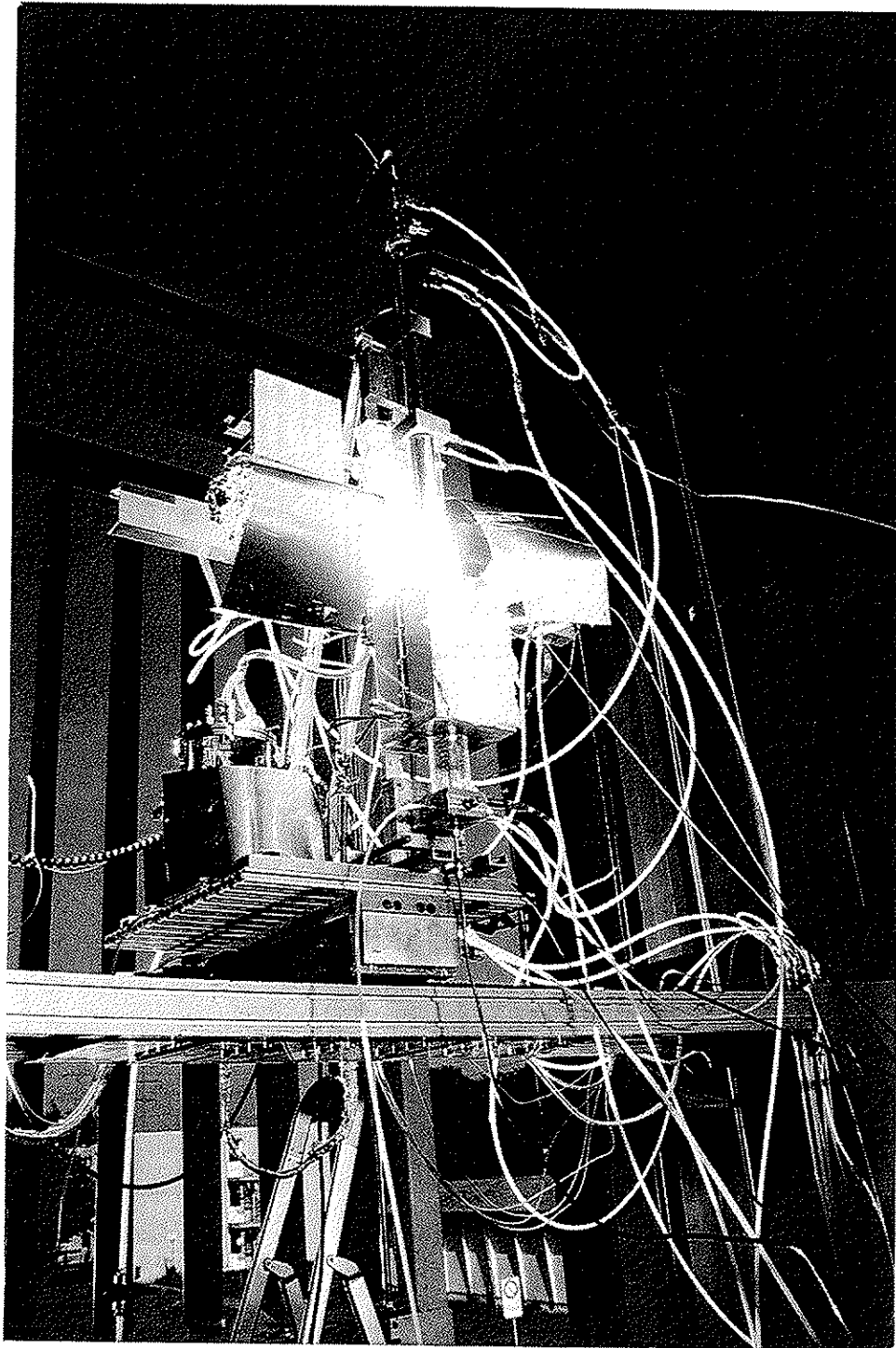
Air; 250 W/cm²



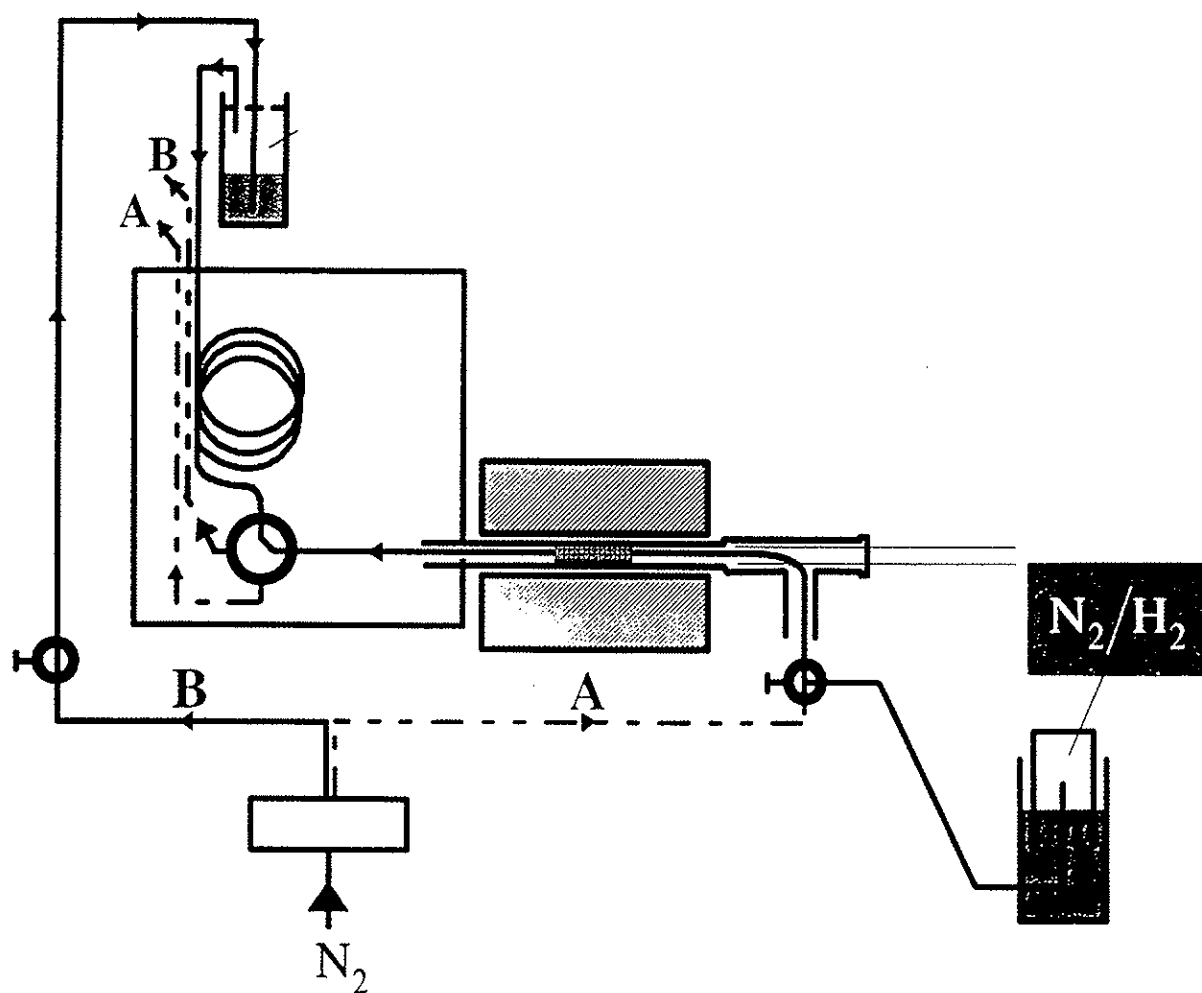
- (113) $\alpha\text{-Fe}_2\text{O}_3$
- (200) Fe_2O_3
- (400) Fe_3O_4

PARTICLE CLOUD FLOW THROUGH REACTOR



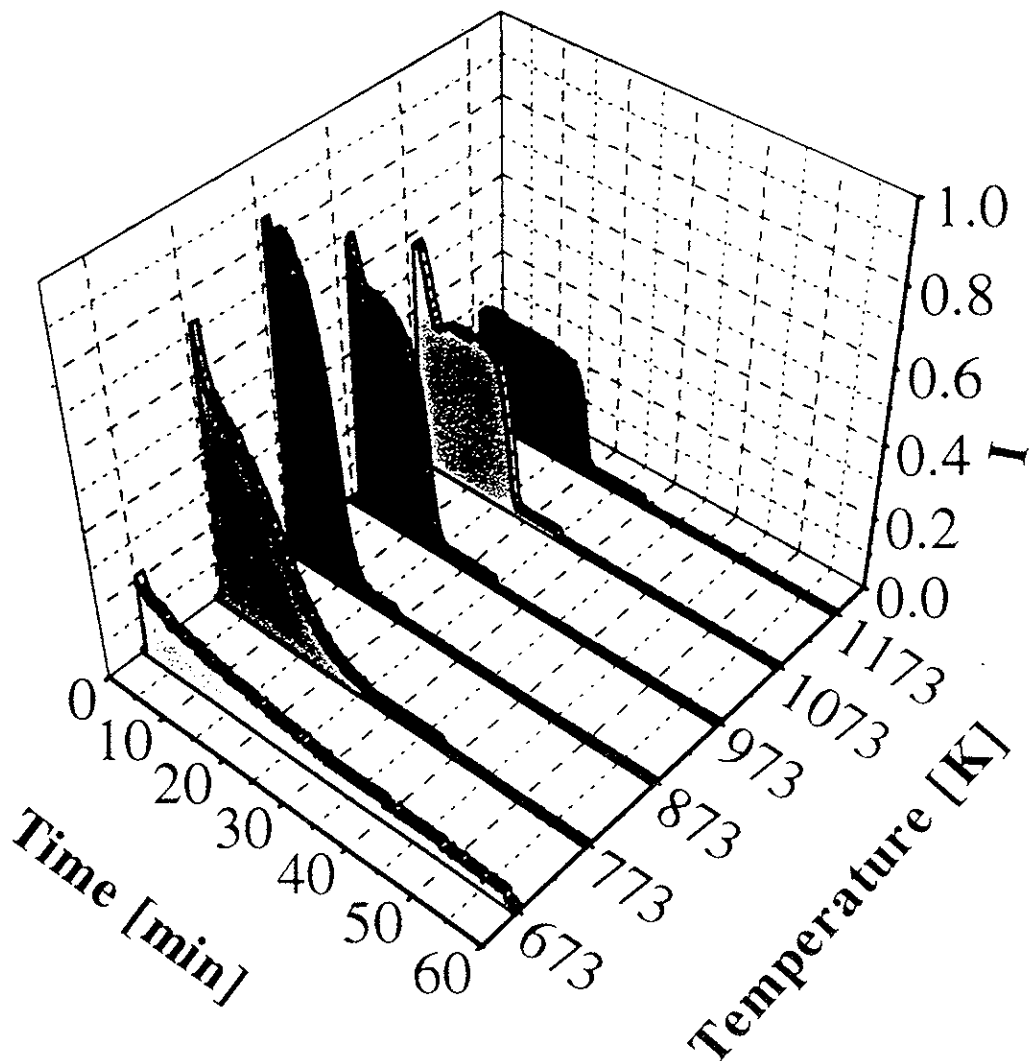


Apparatus to Investigate the Oxidation Kinetics



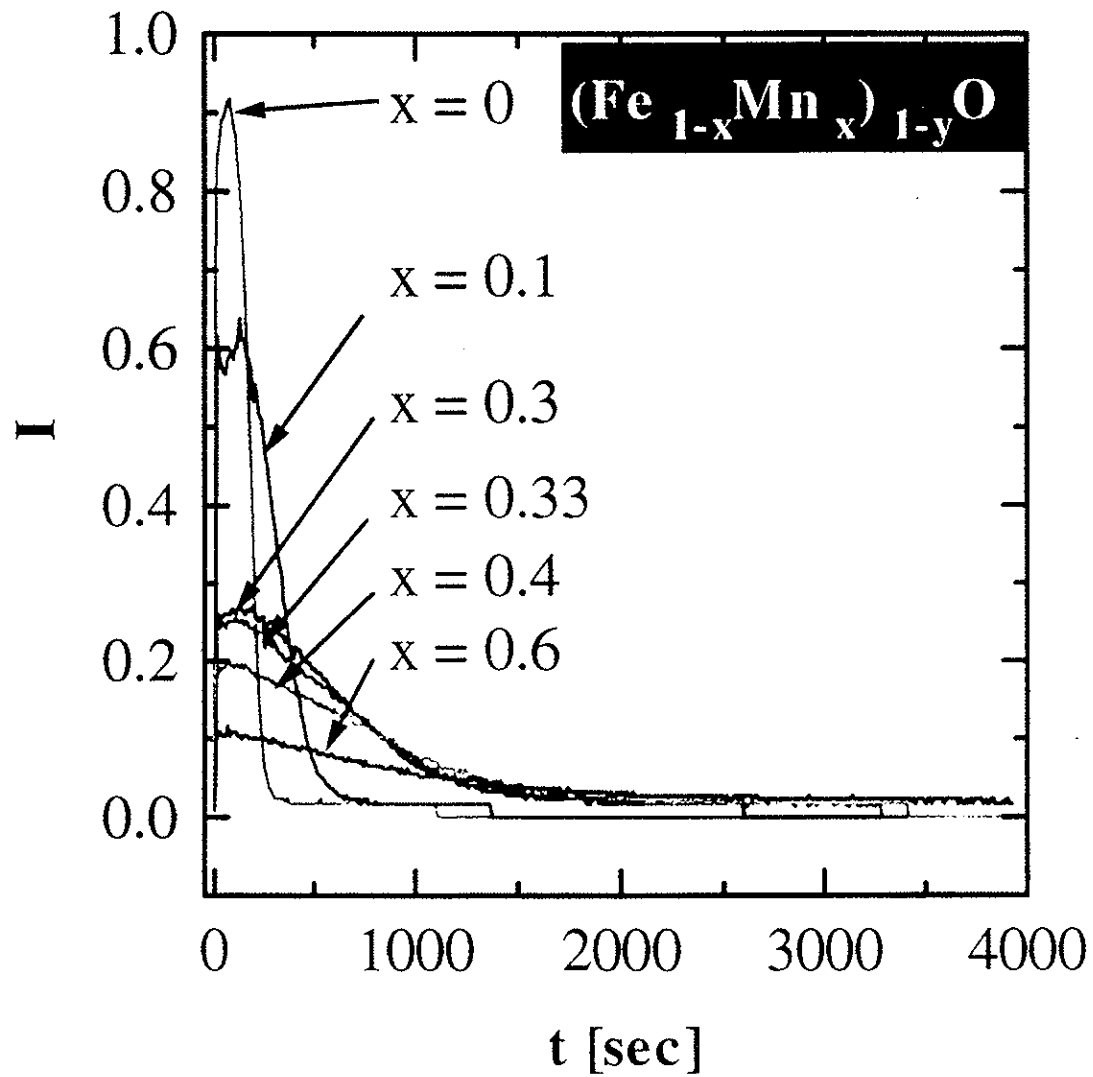
Hydrogen Evolution as a Function of Time and T

Initial Oxide $\equiv \text{Fe}_{0.92}\text{O}$; $T = \text{variable}$, $p(\text{H}_2\text{O}) = 4239 \text{ Pa}$



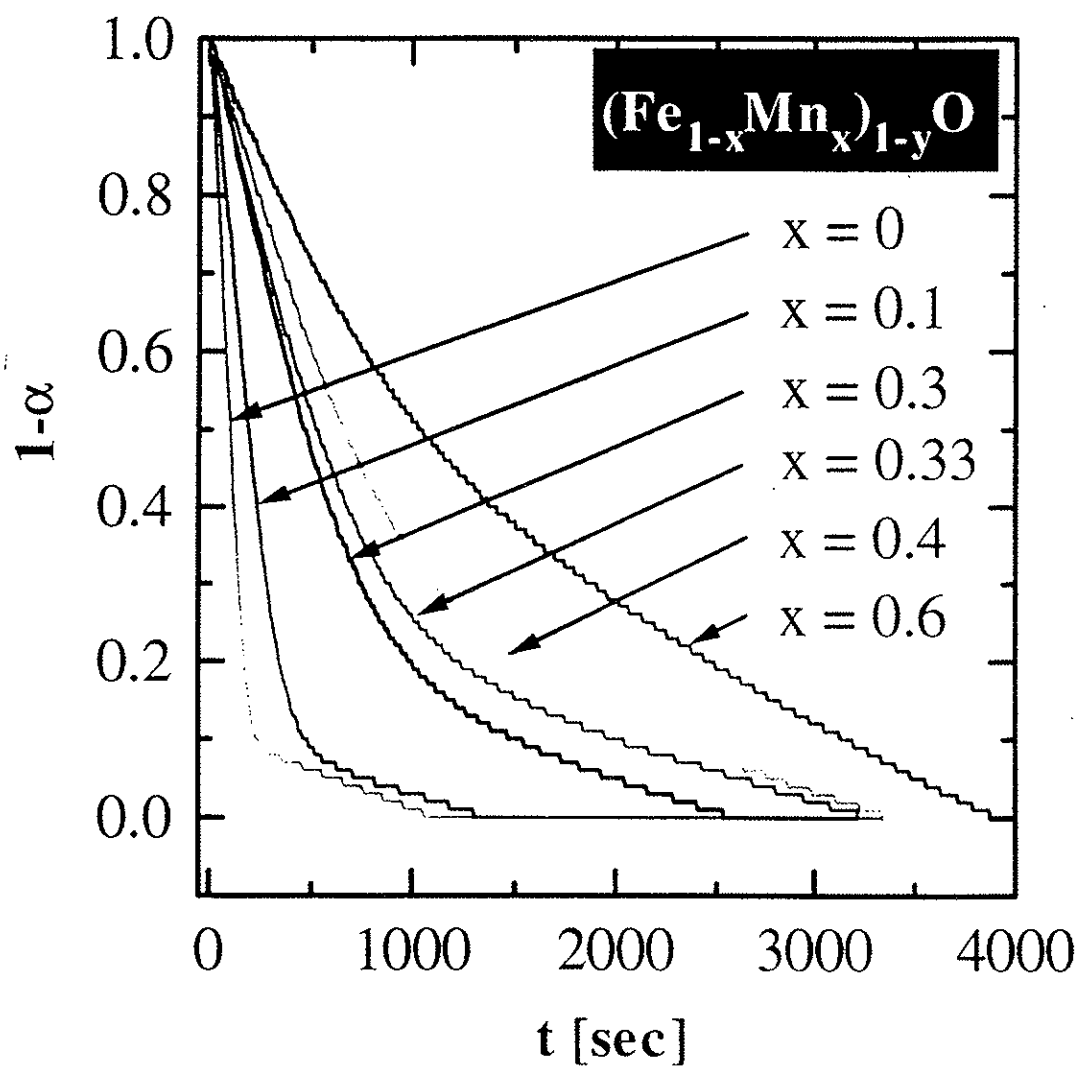
H₂ with Manganowustite-Phases

$$T_R = 873 \text{ K}; p(\text{H}_2\text{O}) = 12330 \text{ Pa}$$



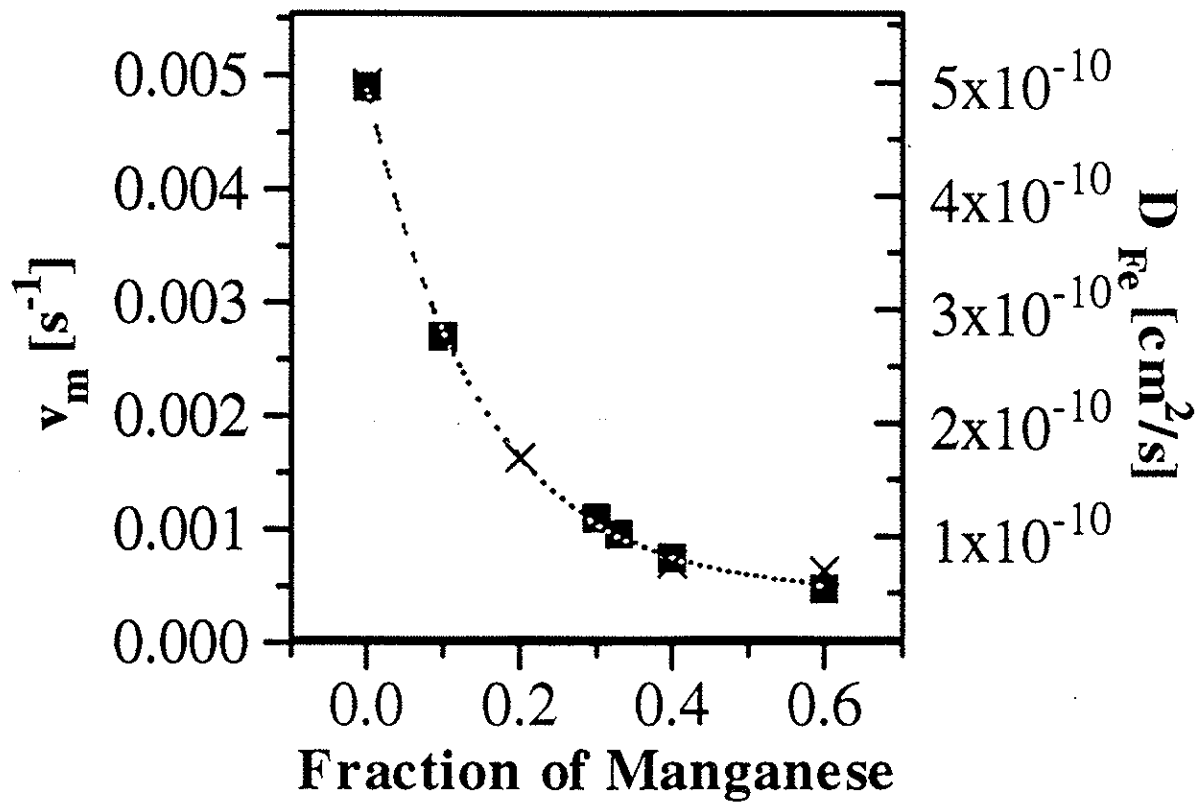
1 - α versus Time

(α = Degree of Conversion)



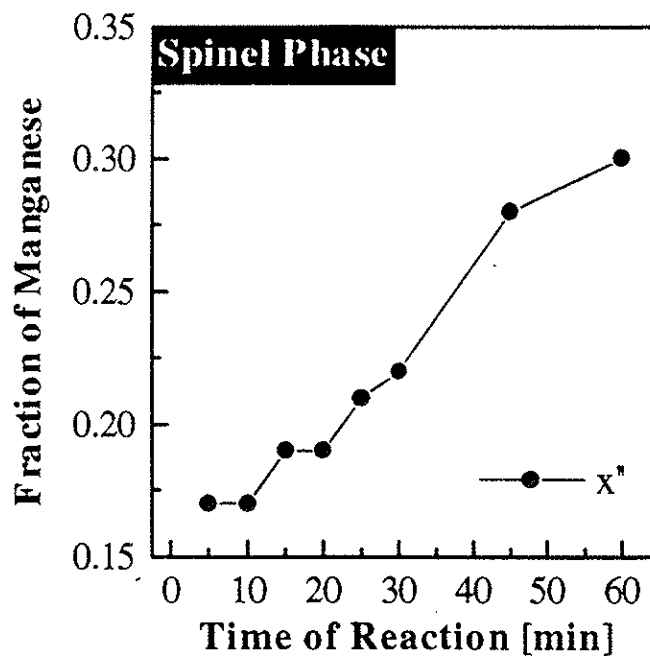
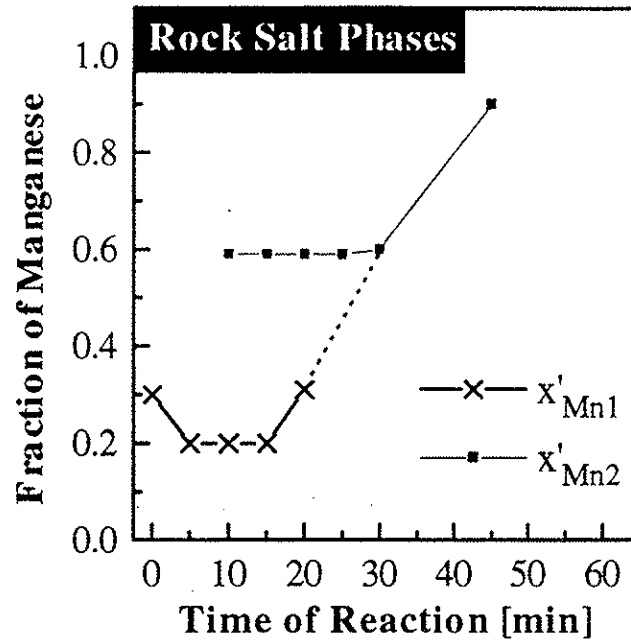
Average Reaction Velocity

$$v_m = 0.00042 + 0.00446 e^{(-x/0.1534)} [s^{-1}] \quad (\sigma = 4.7 \times 10^{-5})$$

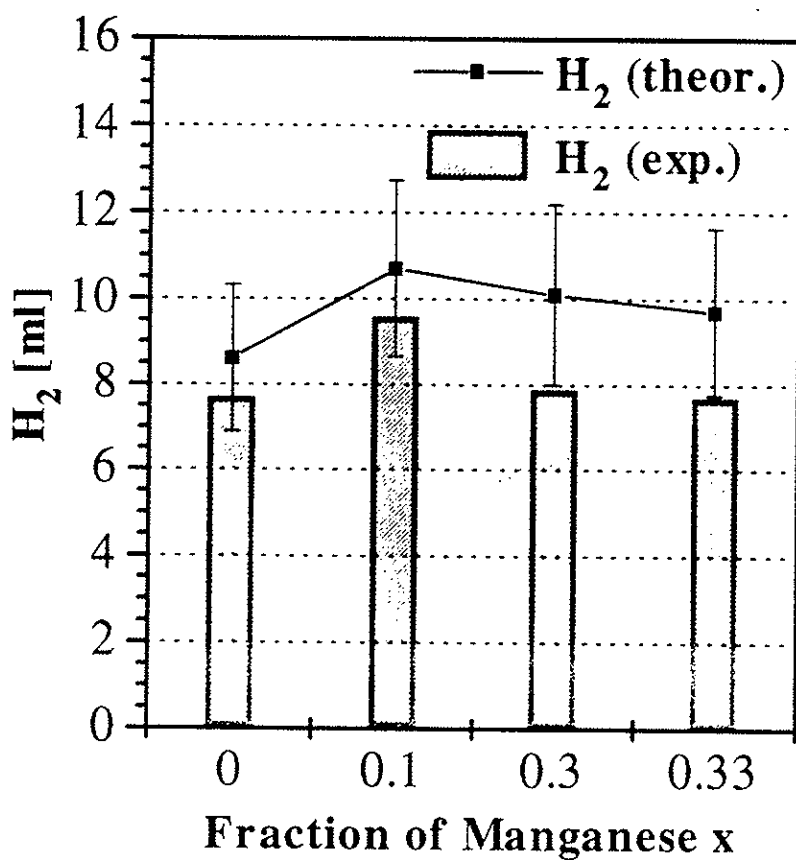
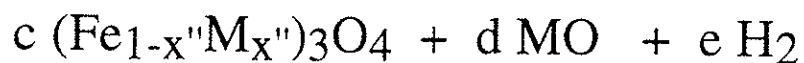
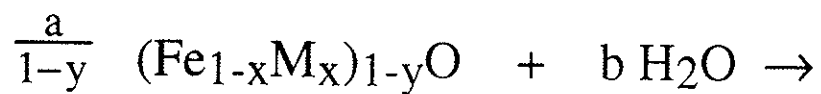


Segregation Processes

$(\text{Fe}_{0.7}\text{Mn}_{0.3})_{0.99}\text{O}$; $T = 1073 \text{ K}$; $p(\text{H}_2\text{O}) = 4239 \text{ Pa}$



Total Amount of Hydrogen



New Opportunities for High-Temperature Solar Chemistry

Michael Epstein
Weizmann Institute of Science
P.O. Box 26
76100 Rehovot
Israel

Most of the R & D efforts at the Weizmann Institute in the area of high temperature solar chemistry, so far, have been devoted to gaseous catalytic reactions. Recent results of the reforming reactions using WIS's tubular receiver and DLR's volumetric reformer will be presented.

The area of interaction between highly concentrated solar radiation and reacting solids is even more challenging, but also, potentially, has long list of applications. The concept of beam down reflective tower opens the possibility for a variety of high temperature receiver / reactor devices for chemical applications.

Three general approaches to handling of solids in highly concentrated solar radiation will be discussed. The first example is gasification of fine coal particles dispersed in liquid drops while a cloud of such drops is moving through a focal zone of highly concentrated solar radiation.

The second approach is indirect and direct fluidized bed solar reactors, illuminated from the top.

The third concept involves solid reacting particles dispersed in a continuous liquid phase at high temperatures.

New Opportunities For High Temperature

Solar Chemistry

M. Epstein
Solar Research Facilities Unit
The Weizmann Institute of Science, Rehovot

Presented at the International Workshop on
High Temperature Solar Chemistry

August 17, 1995

PSI, Switzerland

High Temperature Solar Chemistry

1. Introduction

Recent developments of windowed solar receivers and the optical concept of the tower reflector with its associated concentrating devices open new avenues for high temperature solar chemistry. One of the most challenging directions is the interaction between highly concentrated solar radiation and solid reacting particles. Reactions such as gasification of carbonaceous materials, thermal decomposition of metal oxides or carbonates are of high importance. The reacting particles can be dispersed in gaseous or in liquid phases (i.e. molten salts). Some examples and preliminary test results for these systems are described.

2. Reforming reactions

Catalytic reforming reaction between methane, CO_2 and steam using concentrated solar radiation has been reported by several authors in the last decade^{[1], [2]}. However, only recently, a solar reformer on a hundred kilowatt scale has been coupled with a matching methanator to close the loop in a continuous mode of operation.

During the first half of 1995 experiments were performed with DLR's SCR volumetric reformer at WIS, integrated into the existing closed chemical heat pipe loop.

Summary of some results are shown in Table 1. The system and the receiver's subsystem are shown in Fig. 1,2. Some typical results from the 6th and the 13th of April are shown graphically in Figs. 3,4. Power inputs of up to 280 kwatts and 80% methane conversion were obtained. The entire system is successfully operated. Currently a tubular reformer is under testing.

3. The Reflecting Tower Concept

Although the concept of Reflecting Tower has been mentioned in the literature in the past^[3] it did not succeed to attract much attention due to "impracticality". Today there are good chances for the successful implementation of the concept. Fig. 5 presents the concept schematically. The "Reflecting Tower" consists of a hyperbolic shaped mirror placed on the tower at a certain height such that its upper focus coincides with the aim point of the

heliostats field. This hyperbolic mirror reflects the light down so that its lower focal plane coincides with the entrance aperture to a CPC, whose exit aperture is the receiver's opening. Fig. 6 shows the possible theoretical concentration factors with parabolic dish, regular tower (with heliostats as Fresnel reflectors) and reflecting tower at various angles of sun declinations. From this figure one can see that for large solar tower plants (ratio of field radius to tower height more than 1 or typically 150-200 meters) the theoretical concentrations that can be achieved with the "Reflecting Tower" are much higher than with the regular "Solar Tower". For example, at 30 degrees sun declination one can achieve 22 000 concentration level compared to 10 000 with the classic "Solar Tower". The superiority of the "Reflecting Tower" is even more convincing as one extends the size of the plant and the field. The advantages of the reflecting tower concept are both optical and practical because it enables the placement of the reactor and the CPC on ground level. The tower becomes simpler and cheaper. The chemical plant is built on the ground. Its construction and maintenance becomes much easier.

To illustrate this concept an example design of a commercial scale solar chemical cracker has been performed. The purpose of the plant is to crack thermally 62 000 t/y LPG (Liquid Petroleum Gas, a mixture of n-butane, i-butane and propane) to produce 20 000 t/y ethylene, 9800 t/y propylene and other fuels. The solar power required is 28 MWth into the process. The layout of the heliostats field is shown in figure 7a. The field comprises about 700 heliostats 95m^2 each. The tower height is 125 meters and the shape of the hyperbolic mirror installed on the tower is shown in figure 7b. The area of this reflector is 1483 m^2 and the ratio of the tower reflector area to the heliostats reflective area is 2.2%. An example of the CPC (Compound Parabolic Concentrator) arrangement is shown in figure 8. The reflective area of the CPCs is 1135 m^2 . The reactor design is shown in figure 9. The reactor is of hexagonal shape with 13 m on each side. The radiation enters through 7 openings in the ceiling of the reactor. The reactor includes 240 cracking tubes. The radiative heat transfer inside the cavity, the kinetics and chemistry calculations have been performed to design and assess the performance of this reactor.

4. Solar gasification of organic solid particles dispersed in liquid drops

The main obstacles for using solar energy for industrial processing of solids are:

- Transportation of solids
 - dust sedimentation on optical components (reflective surfaces) reduces reflectivity and increases maintenance cost.
 - dust increases the attenuation of the reflected concentrated radiation in the atmosphere.
- Handling and Feeding Systems of the Solid Particles
 - Expensive and complicated mechanisms and moving parts in hot environment (conveyors, vibrators, etc.)
 - Complicated feeding system (i.e. screw feeders) of the solid particles (i.e. coal, wood, etc.) into the hot reactor (pneumatic feeders are forbidden)
- Generating and injection of high temperature steam
 - superheated steam at a temperature close to the reaction temperature (i.e. 900°C) is required.

A new concept for solar gasifier is introduced to overcome most of these obstacles.

The concept involves the interaction between very high concentrated solar radiation and coal particles dispersed inside water drops. A slurry of coal in water is prepared and piped in a well-known technology. (Coal-water mixtures typically 60-70% by mass, particles sizes of 100-300 microns with stability dispersants 0.2-0.5% by mass are piped in many projects around the world. The longest and largest slurry pipeline in operation is the 440 km, Black Mesa coal pipeline in Arizona USA. It transports 4.5 million t/y in 457mm pipe diameter.) At the solar site the solid content is adjusted in an agitated tank to the conditions required by the solar gasifier by adding water. Typical composition range is 10-30% solids by mass. The slurry is pumped and injected into the solar reactor through an array of pressure nozzles which create a cloud of drops at the focal volume. A drop of typical average diameter of 2 mm can contain about 100 particles of 200 microns in the case of 10% slurry. When a drop is exposed to a high level of concentrated solar radiation the black particles are heated rapidly. At a critical radiation intensity above a certain

threshold level a small vapour film is created around the particle. At this critical flux the heat absorbed by the particle surmounts the thermal losses by radiation, convection and conduction into the surrounding water film. Once the vapour film is formed the heating rate is suddenly increased and reaches 10^5 - 10^6 °C/second and the particle temperature is increased dramatically. Also, when the film of vapour is created the drop explodes and its fragments behave as new, smaller bodies which absorb the radiation. Nevertheless, from preliminary experiments, because of the rapid heating rate, the particles reaches the temperatures required both for devolatilization and gasification processes. The particles react with the water vapour in their vicinity and are gasified. The behaviour of a single drop and particle are illustrated in Figure 10. The cloud of drops behaves similar to a cloud of particles. One of the main problems is to obtain long residence time, enough for heating the particle and reacting with the vapour. In preliminary experiments this has been achieved in "impinging jets reactor". In this type of reactor two or four jets of drops were sprayed through pressure nozzles from opposite directions so that the drops were slowed down in the focal zone of a solar beam. Solid cone and whirl chamber nozzles were used (see Figure 11^[4]). Other types of reactor such as cyclone can be used as well. The experimental setup is shown schematically in Figure 12. Gasification of charcoal was obtained in this type of reactor. A slurry of 1% in mass charcoal in water was used. About 50% of the charcoal was gasified in a once-through mode of operation. The unreacted drops remain mostly cold, are removed from the reactor and can be recycled.

The advantages and disadvantages of this concept are:

- Advantages
 - Easy transportation as a water slurry
 - Preparation of the solids can be done far from the solar site. Dust is prevented.
 - Cheap, simple feeding system such as spray pressure nozzles.
 - Minimizing the amount of surplus of steam above what needed for the reaction.
 - Very high energy fluxes can be absorbed.
 - Catalyst can easily be added or dissolved in the liquid
 - The receiver's housing remains cold. It has low thermal inertia and therefore, shorter start-up time.

- Disadvantages
- Requires windowed type reactor.
- Short residence time.
- Shadowed drops inside the cloud.
- Agglomeration phenomena.

5. Gasification of organic solids in molten salt medium

The beam down concept raises again the possibility of solar gasification of coal particles dispersed in a molten phase. Past experiments done with conventional heating show good heat transfer properties and successful results were obtained for the pyrolysis stage in molten carbonate salts [5]. In the case of direct solar illumination of the salt there is advantage for transparent melt where the coal particles can absorb the light and reach higher temperature. First, the coal is pyrolyzed, volatiles and tars are released as bubbles out of the liquid, then the remaining charcoal is heated up and can reduce the molten salt to release the pure metal through the gasification process. Fig. 13 shows schematically a solar coal gasifier using molten salt medium.

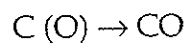
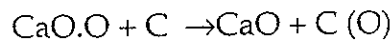
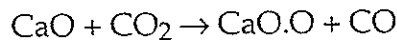
6. The Use of Reflecting Tower in few fluidized bed reactors

Fluidized bed reactors of various types (moving bed, classical fluidized bed and circulating bed) can be used for several applications in the high temperature solar chemistry area. Most of them were using side window which was problematic for coal gasification and pyrolysis applications. The "Reflecting Tower" concepts open new options for the design of this kind of solar reactors. One example is limestone (CaCO_3) calcination to form lime (CaO). The cyclone type reactor is most suitable. The window is not required. Different types of commercial cyclones are shown in Figure 14. All of them work at atmospheric pressure. A cyclone can be placed on the ground, equipped with CPC on top of the clean-gas outlet. The limestone particles are exposed to direct illumination of solar radiation (see Fig. 15). This type of reactor can be used also for thermal decomposition of metal oxides. However, when pyrolysis and gasification reactions are considered the fluidized bed reactor should preferably be equipped with a quartz window and means must be provided to avoid any volatiles or carbon particles to reach the window. This has been demonstrated for small size windows (20 cm in diameter) with steam jets flashing the window thoroughly. This can be achieved much easier

with horizontal window at the top of the reactor with particles floating upwards, then with a side window. A way to avoid a window in a solar fluidized bed gasifier is shown in Figure 16. The reactor is an annular vessel. A typical module will have internal diameter of 4 meters and 3 meter height. The top of the reactor is equipped with a CPC. The solar beam entering the internal volume of the reactor from top through an opening of 3 meters in diameter. The particles are fluidized in the annulus. The heat for the reaction is supplied by conduction through the internal wall and by convection and radiation into the bed. The heat transfer to a fluidized bed from hot and radiating wall as reported in the literature [7] can reach values of 1000-1300 w/m²K. With average bed temperature of 850°C, sufficient for steam gasification of coal, biomass and oil shales, a heat flux of 100 kW/m² can be applied on the internal wall. A reactor module having the size mentioned above is suitable for 4 MW heat into the reaction equivalent to the processing of 1.5 t/h of brown coal.

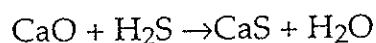
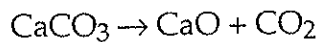
An interesting application for the annular solar gasifier is the gasification of a mixture of low grade coal and oil shales. Two effects are achieved simultaneously:

- a. Catalytic effect of calcium carbonate

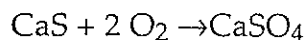


where CaO.O is a surface peroxide and the rate determining step is the release of the CO from the carbon structure. Increasing the partial pressure of the CO₂ decreased the rate of gasification indicating that the oxide is the active species.

- b. Reduction of sulfur release to the atmosphere. Limestone is calcined to form lime (CaO) , which reacts with sulfur compounds according to:



After removal of the ashes, in the presence of oxygen CaS is oxidized according to:



In conclusion, before a large enough window is developed, a different design can be conceived and built in relatively short time. An annular fluidized bed reactor where the internal wall is heated by the solar radiation and the heat is transferred into the bed through the wall by conduction or by other means such as heat pipes etc. , penetrating through walls into the bed.

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- [2] Boehmer, M., U. Langnickel, J.A. Rodriguez, M. Sanchez, "Solar Steam Reforming of Methane, "Proc. Biennial Congr. Int. Solar Energy Soc., eds. M.E. Arden, S.M.A. Burley, and M. Coleman. Denver, CO, August 19023, 1991, vol.1, Part II, Pergamon Press, Oxford, pp. 828-833, 1991.
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- [7] Cheremisinoff, Nicholas P., editor: Handbook of Heat and Mass Transfer" Vol. 1 Chapter 18, p. 609, Gulf Publishing Company Book Div.

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Table 1

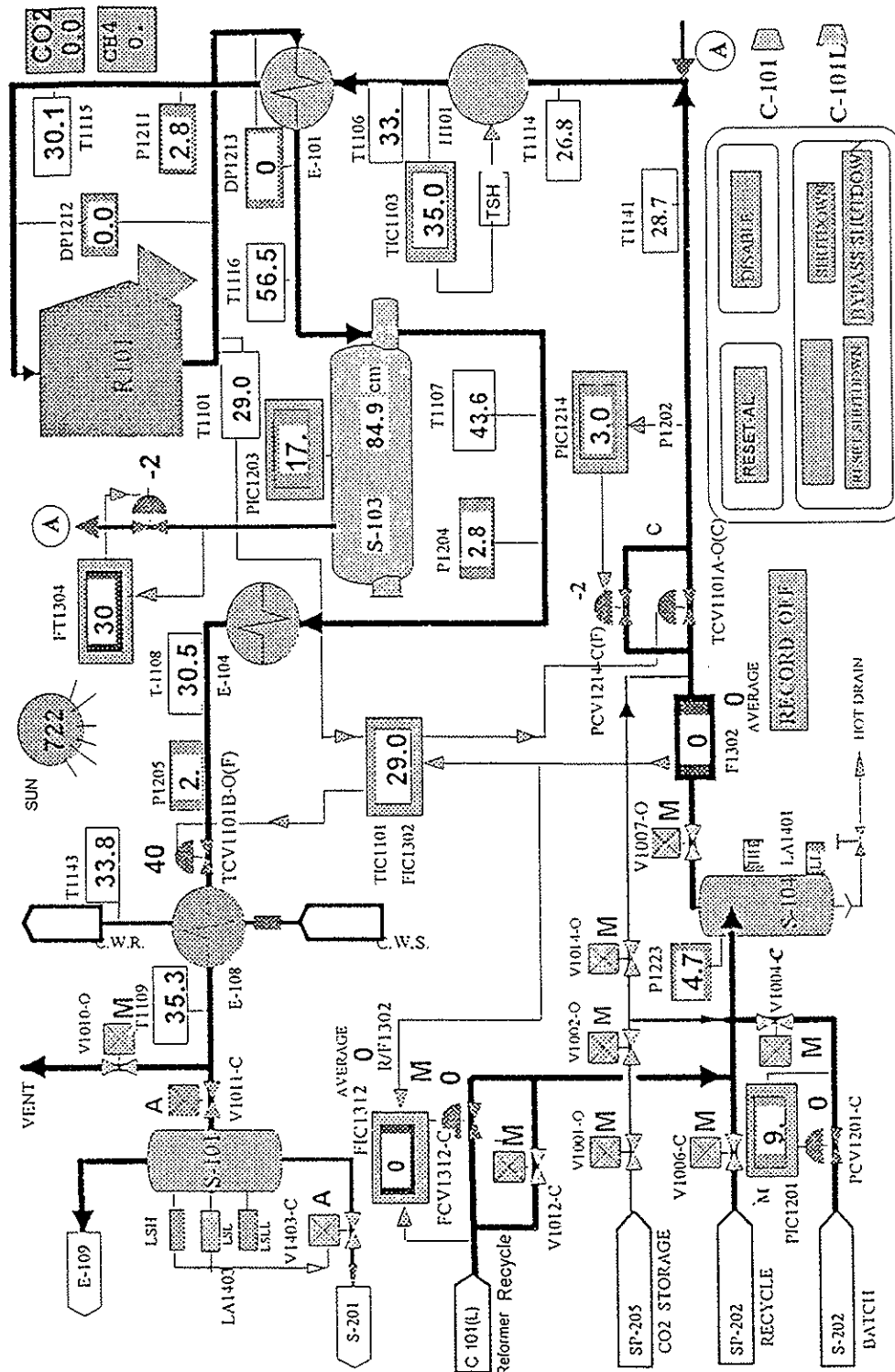
Summary of test results for the DLR's SCR
at the WIS's Solar Chemical Heat Pipe Facility

January - June 1995

Date	Time	Flow	Temp, °C		Methane Conversion, %		Power
1995		kg/hr	in	out	Total	One-pass	k W
24.1	1414	379	385	654	47	37	131
24.1	1453	360	401	655	50	36	116
26.1	1414	444	421	717	72	54	174
26.1	1431	452	436	708	66	48	162
26.1	1523	445	440	726	70	51	182
27.2	1320	457	417	704	60	43	175
27.2	1524	453	419	731	70	43	163
28.2	1455	406	426	729	62	51	203
28.2	1534	402	431	746	70	24	123
14.3	1237	432	427	720	82	65	167
20.3	1251	435	418	703	62	21	96
20.3	1334	405	435	719	71	57	162
20.3	1354	433	440	697	61	46	159
20.3	1445	408	419	696	64	53	185
21.3	1140	464	440	704	66	56	225
21.3	1310	458	431	681	58	49	217
21.3	1413	444	447	723	70	63	235
28.3	1142	448	407	742	72	34	134
28.3	1321	455	411	710	58	39	164
28.3	1446	452	421	731	63	55	222
6.4	1332	675	409	717	71	65	286
6.4	1434	633	419	730	80	68	252
13.4	1117	536	433	767	86	42	144
25.4	1329	467	416	740	81	39	127
25.4	1431	466	425	727	77	64	196
26.4	1136	477	445	773	77	60	193
26.4	1321	472	451	758	77	69	225
26.4	1406	466	448	749	75	66	218
27.4	1144	418	460	769	83	51	133
27.4	1236	456	433	747	70	28	130
27.4	1406	454	437	720	65	54	216
Design conditions		341	500	800	80		280

WIS REFORMER PLANT

FIGURE 1:



DLR REFORMER/RECIERVER

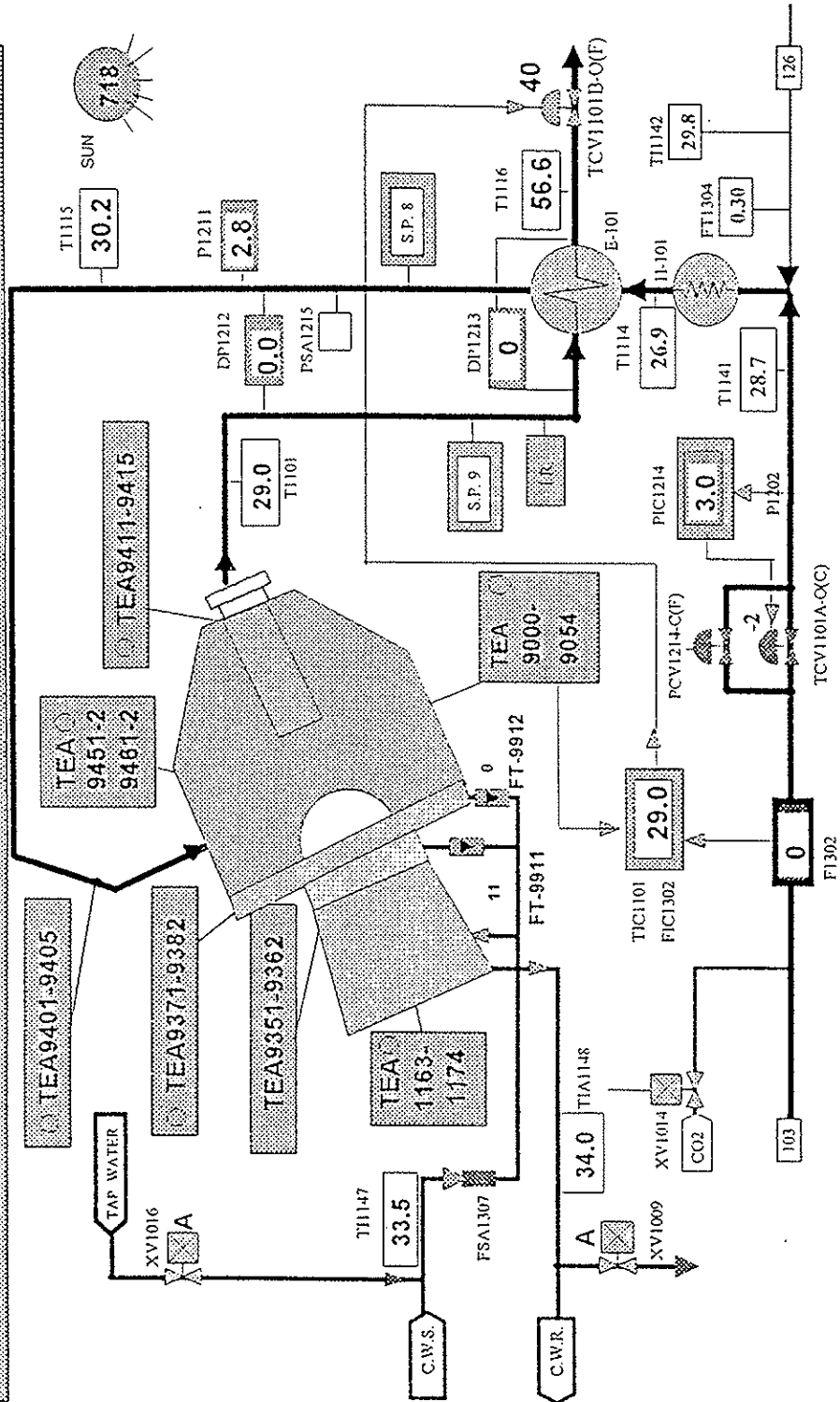
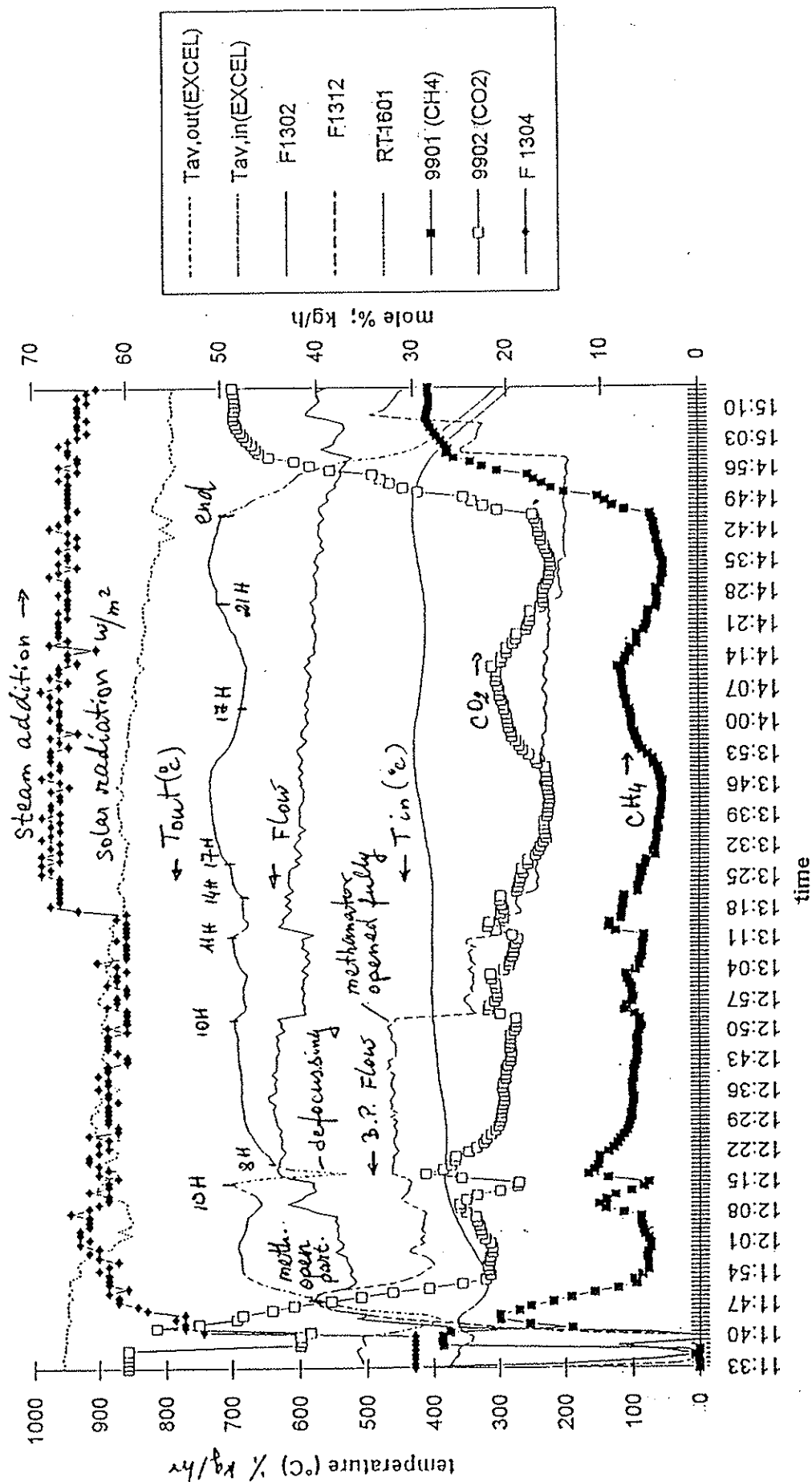
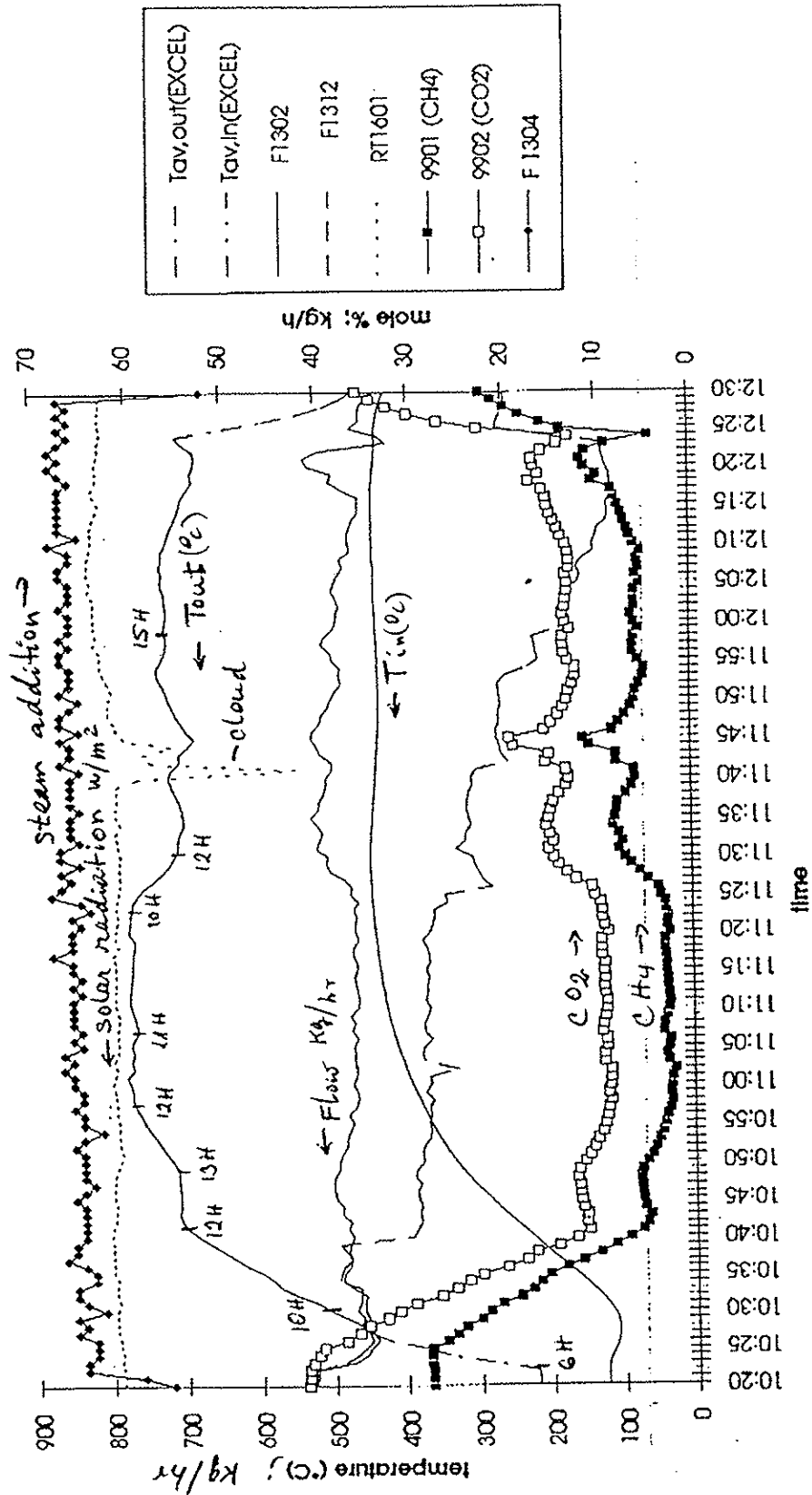


FIG. 3: SCR chemical test overview (Plot 13a)



TST0604.XLS date: 06.04.95

FIG.4: SCR chemical test overview (Plot 13a)



TST1304.XLS date: 13.04.95

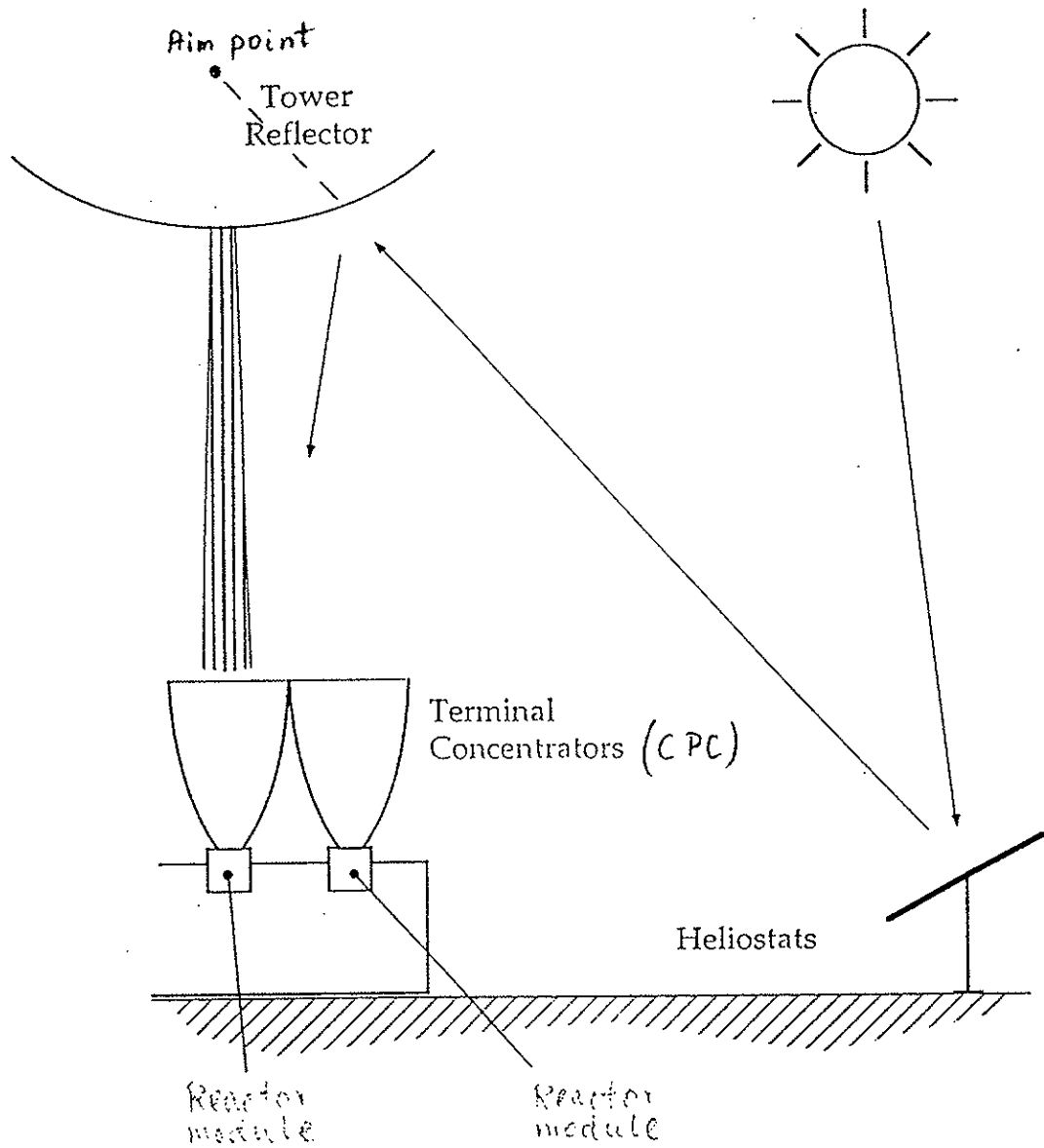


FIG. 5 THE OPTICAL CONCEPT OF "SOLAR TOWER REFLECTOR"

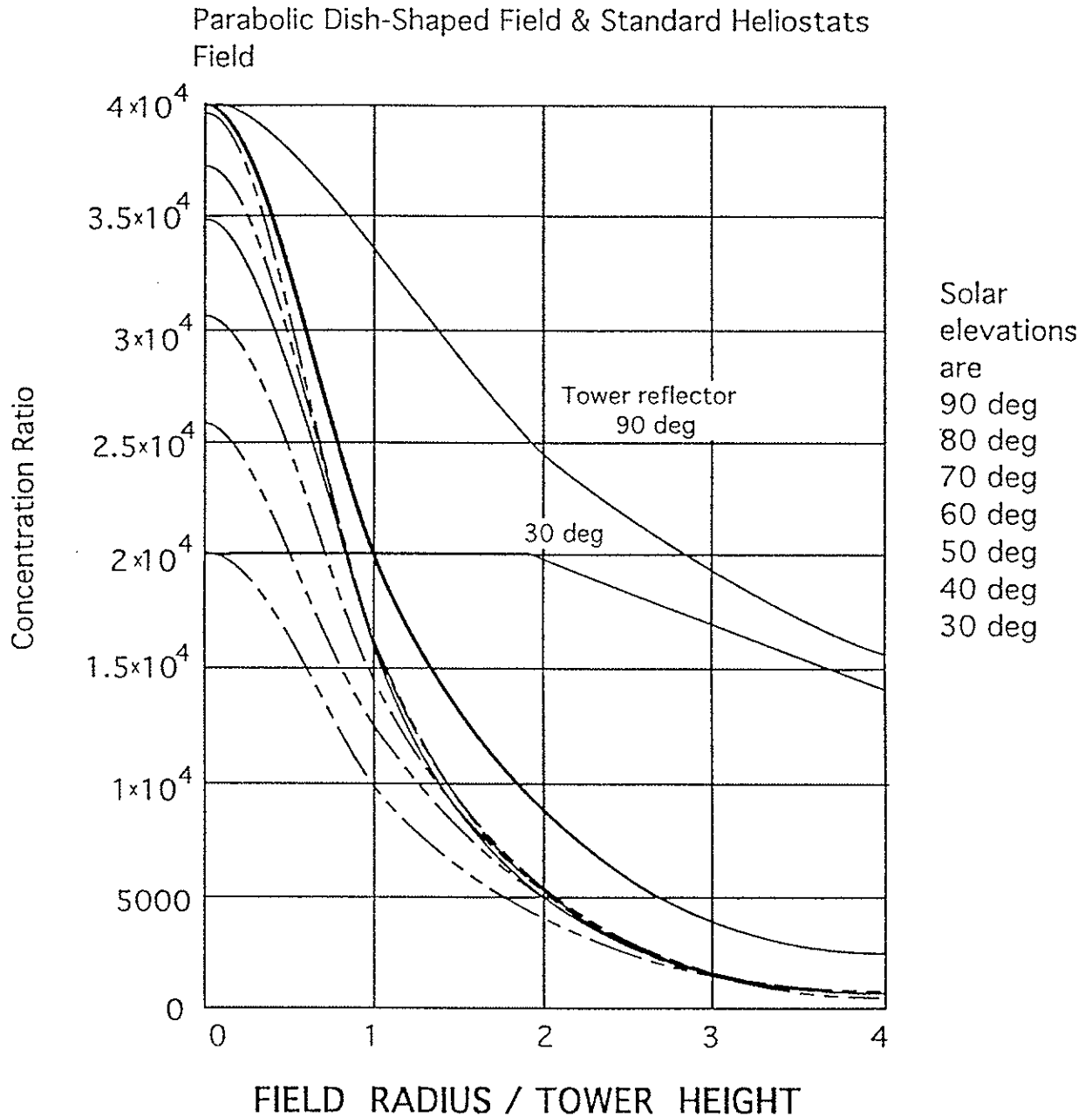


Figure 6 Maximum (ideal) concentration factor achievable at the lower (near ground level) focus of a symmetrical surrounding central receiver field with beam down optics, using a parabolic-shaped and Fresnel-type reflectors, which are illuminated at various elevation angles. Ideal secondary concentrators are used.

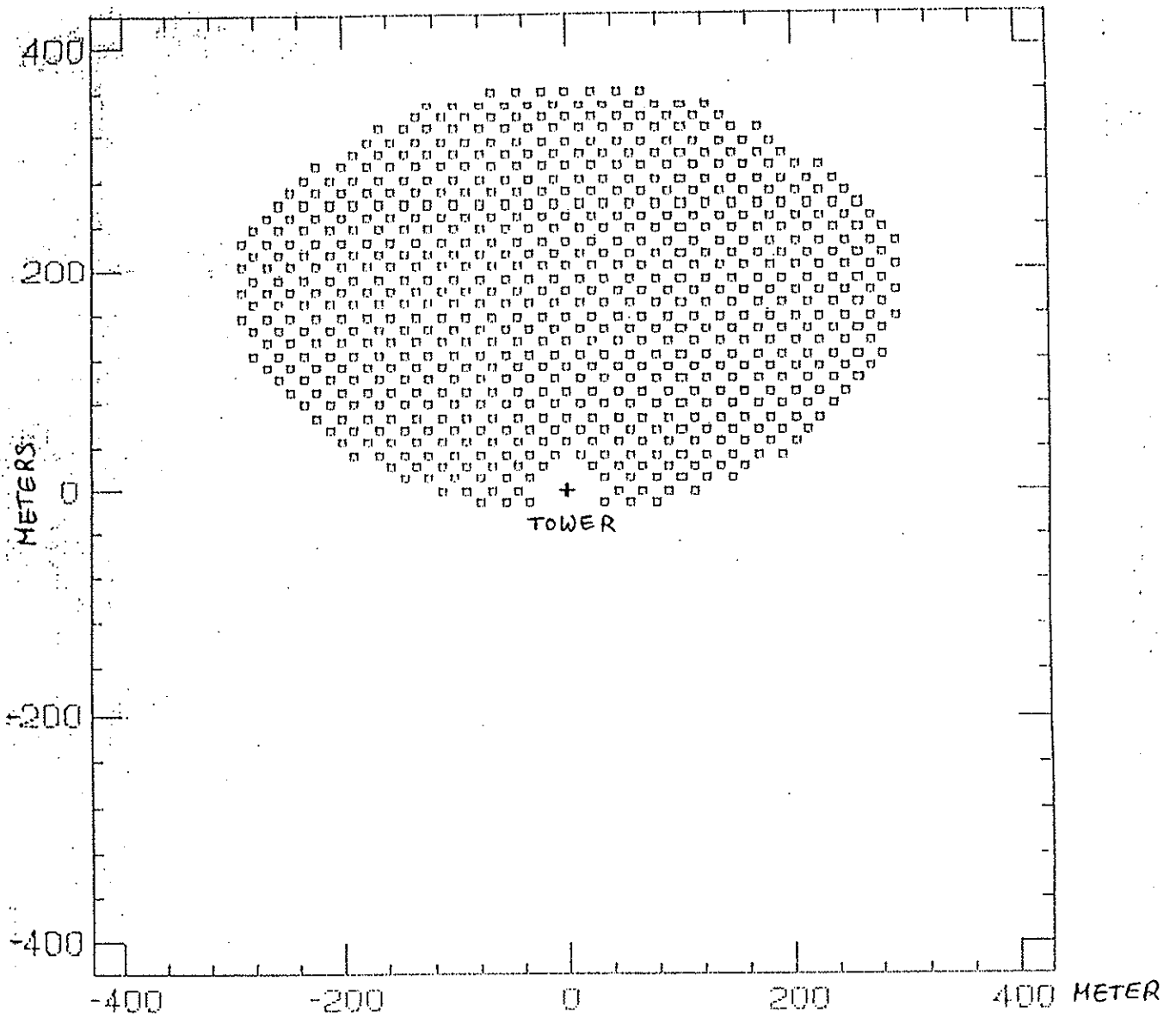


Fig.7a: Heliostats Field layout for 700 units, designed for 28 MWth net into LPG solar cracker.

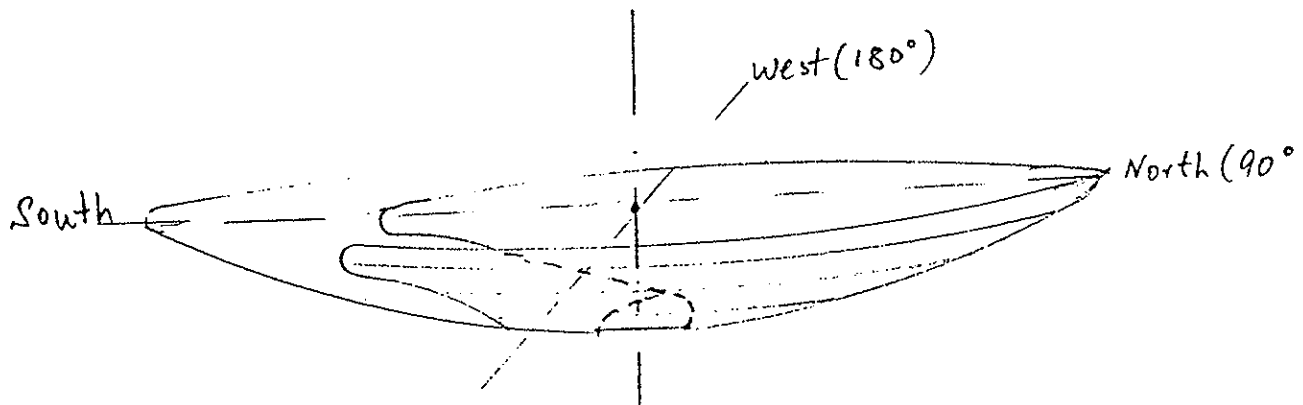


Fig. 7b: Shape of the hyperbolic tower reflector
60m in diameter and 1483m^2 reflective area.

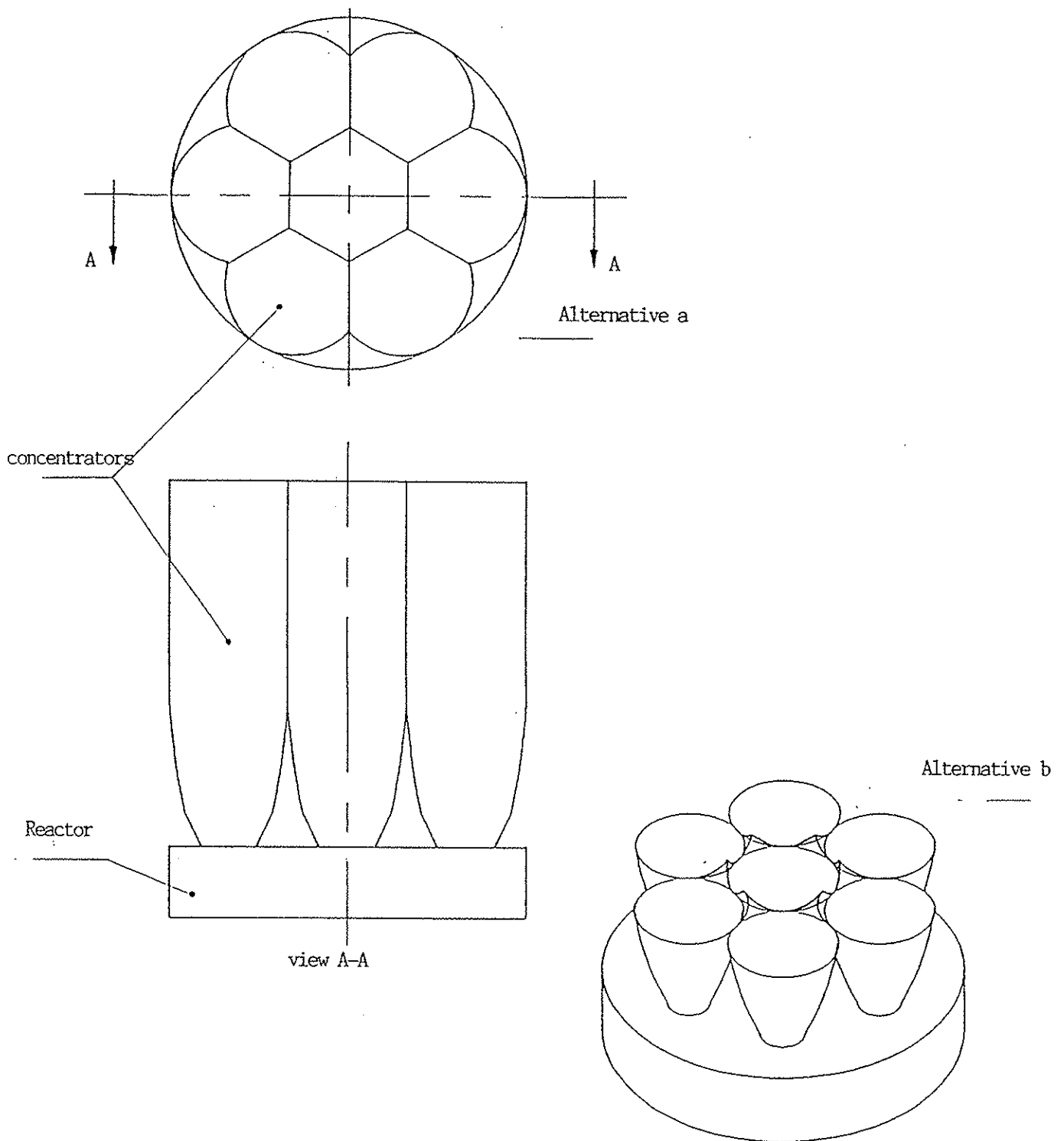


FIG. 8: Arrangement of 7 CPC units placed on the ceiling of the reactor vessel,

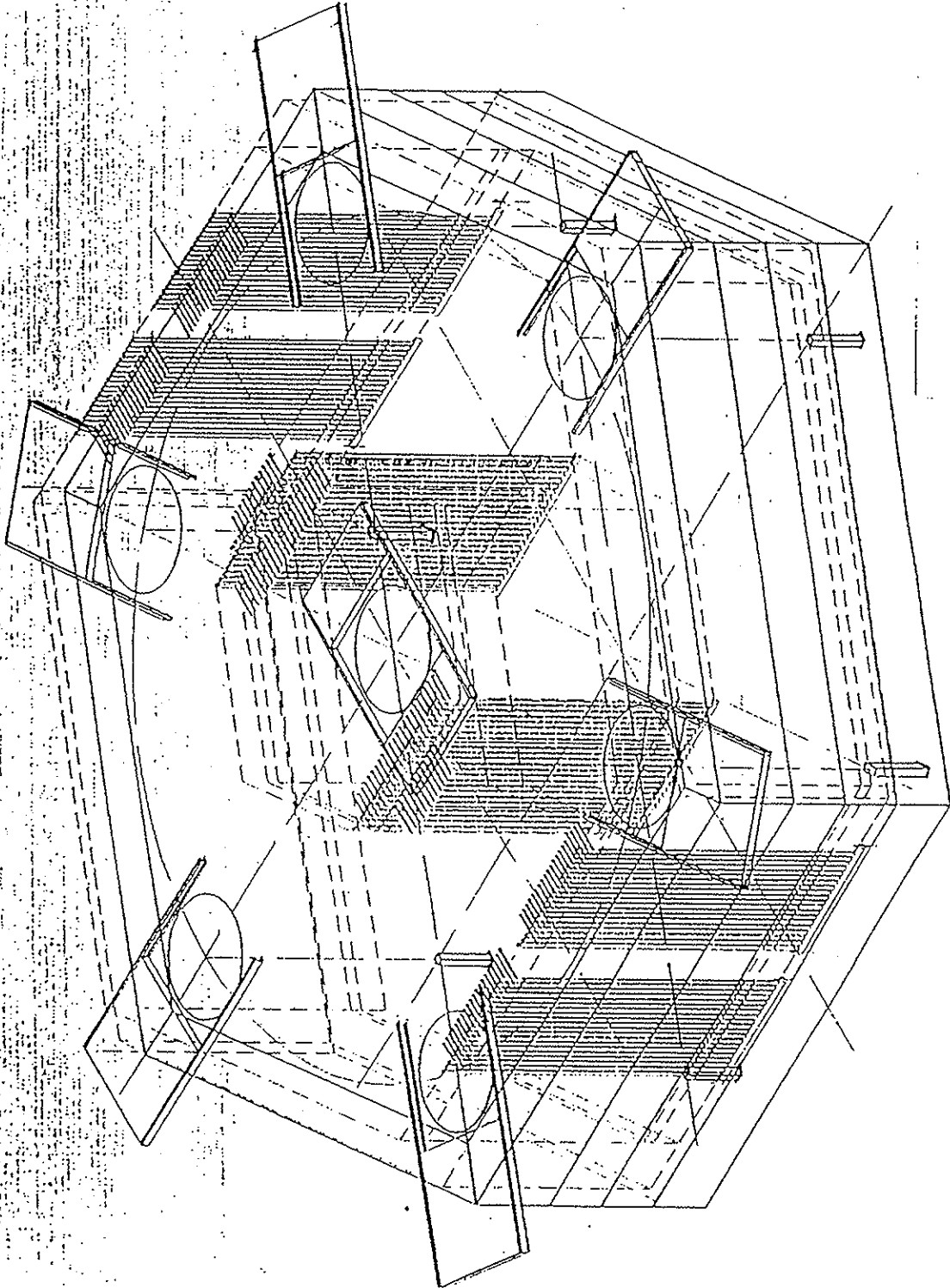


FIG. 9: LPG solar cracker.

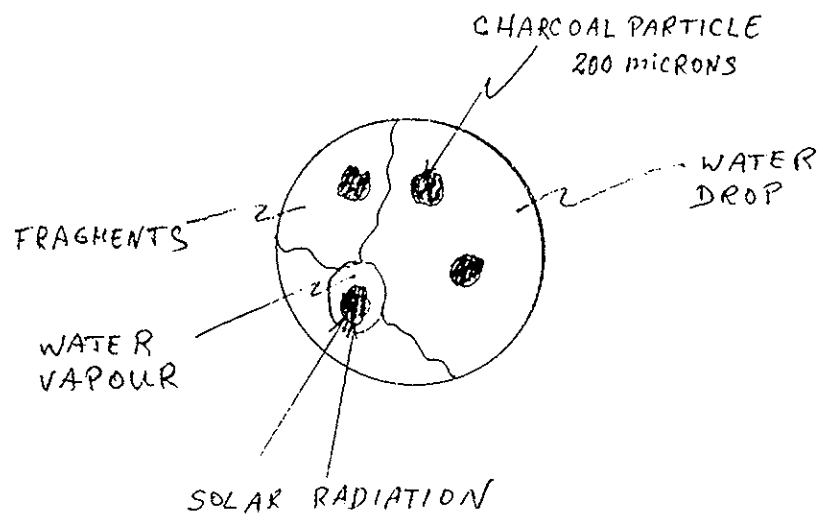


FIG. 10: Water drop with charcoal particles under high solar flux.

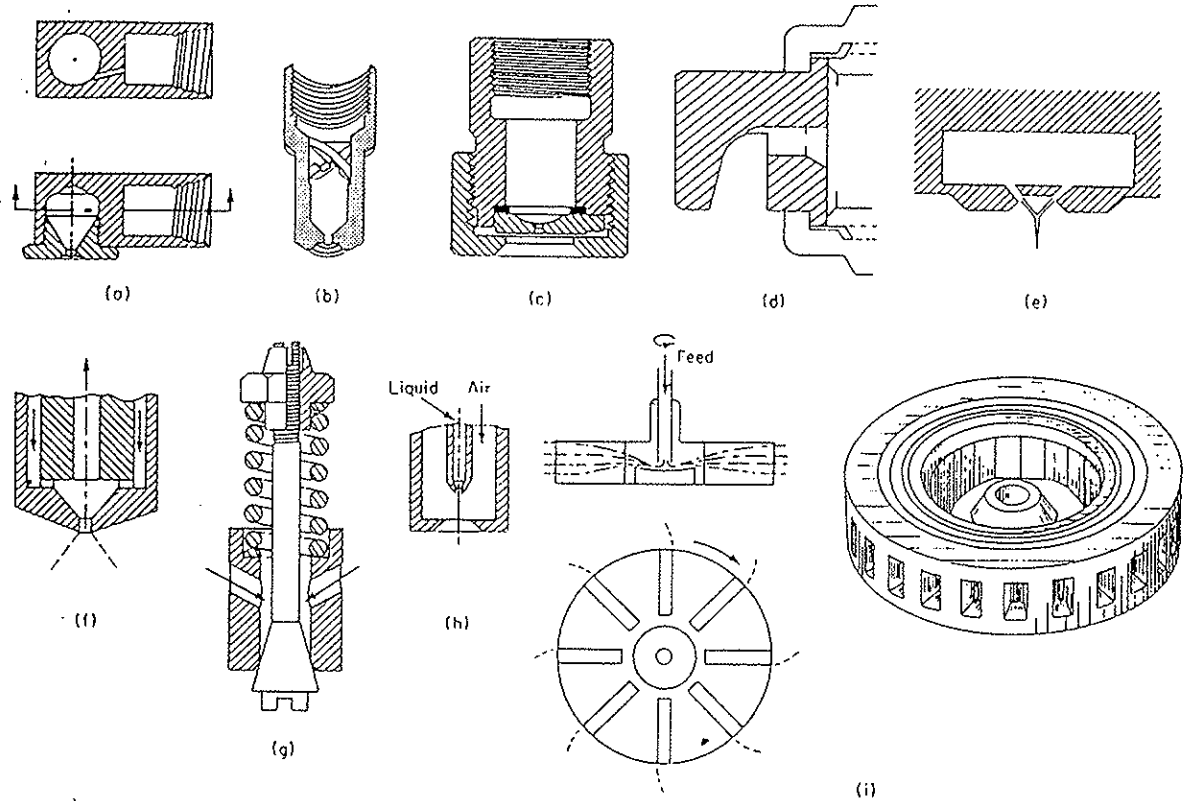


FIG. 18-86 Characteristic spray nozzles. (a) Whirl-chamber hollow cone. (b) Solid cone. (c) Oval-orifice fan. (d) Deflector jet. (e) Impinging jet. (f) Bypass. (g) Poppet. (h) Two-fluid. (i) Vaned rotating wheel. (a), (b), (c), (f), (h), and (i) From Dombrowski and Munday, *Biochem. Biol. Eng. Sci.*, 1968. (d) and (g) Delavan Corporation. (e) Shuttle & Koerting Division, Amelck, Inc.

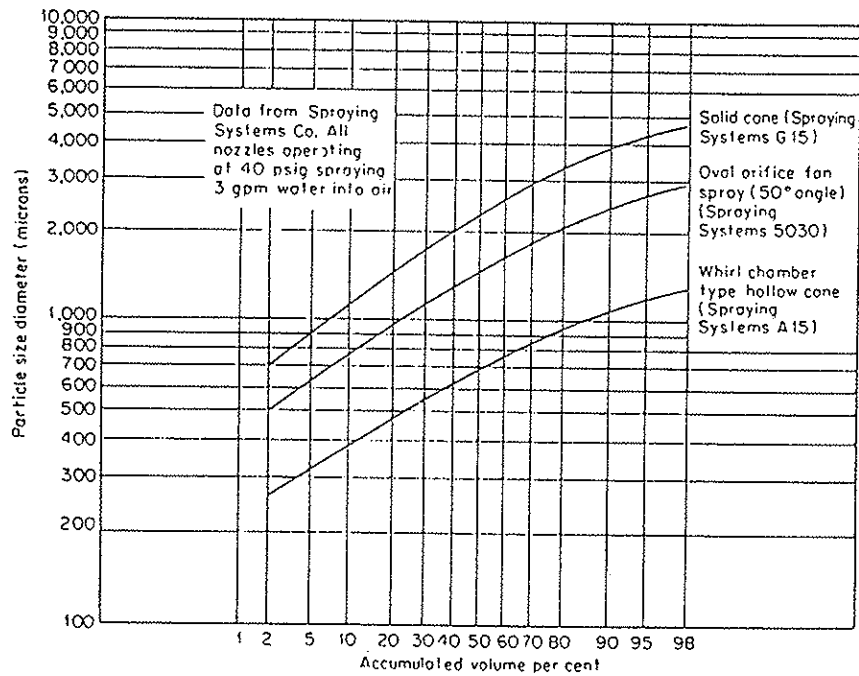


FIG. 18-87 Droplet-size distribution for three different types of nozzles. To convert pounds per square inch gauge to kilopascals, multiply by 6.89; to convert gallons per minute to cubic meters per hour, multiply by 0.227. (Spraying Systems Inc.)

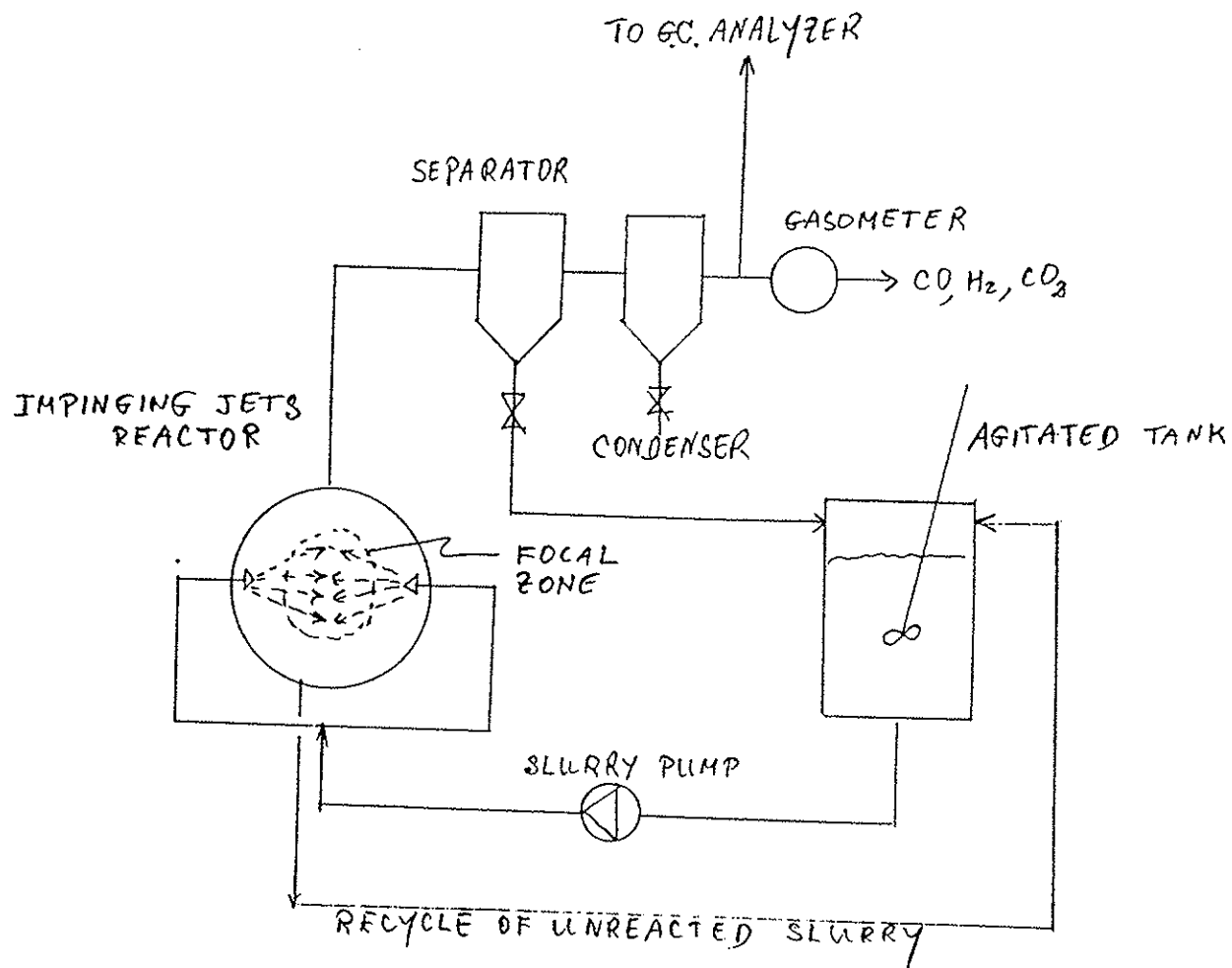


FIG.12: Experimental set up for solar gasification of coal dispersed in a drop reactor.

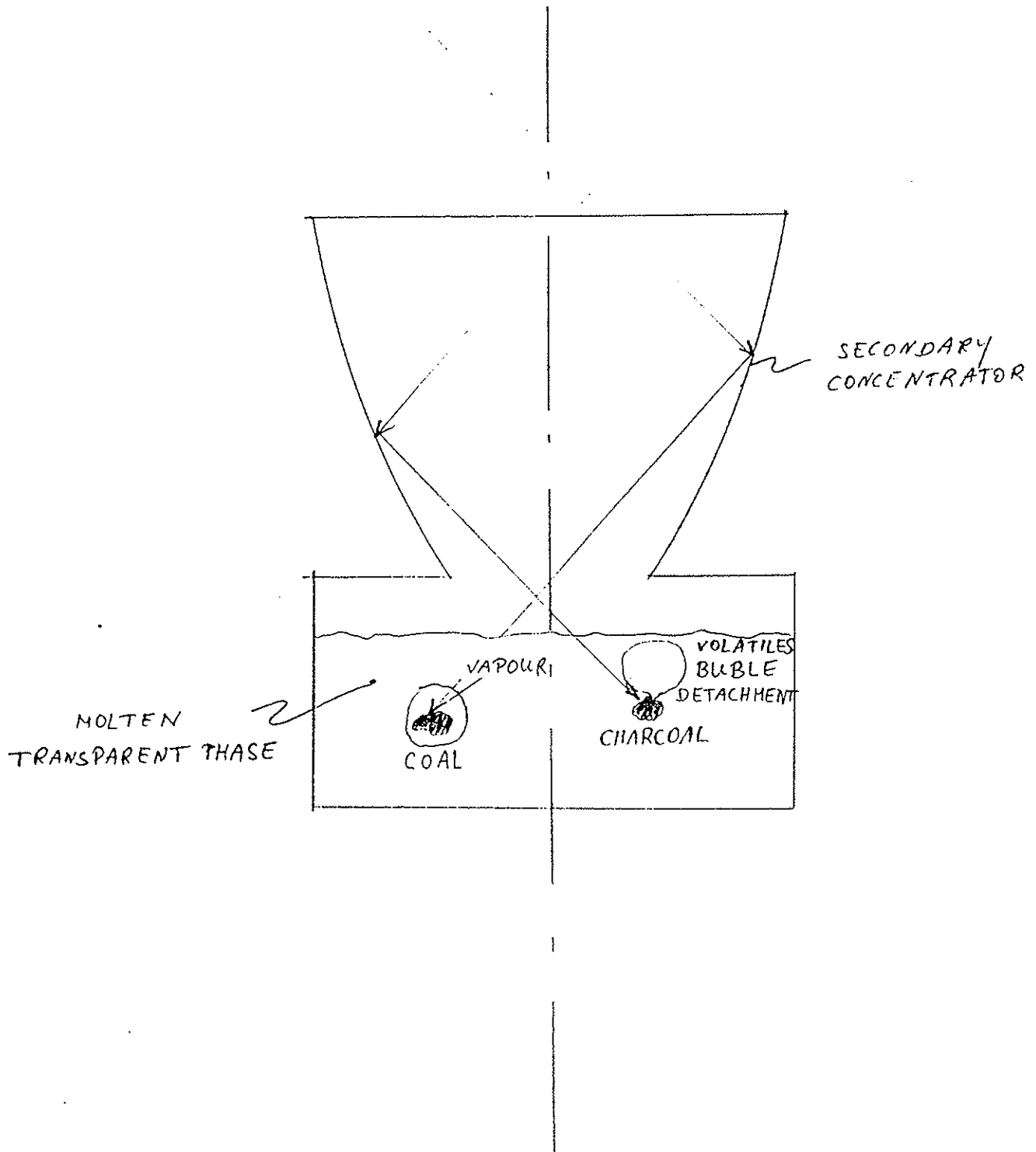
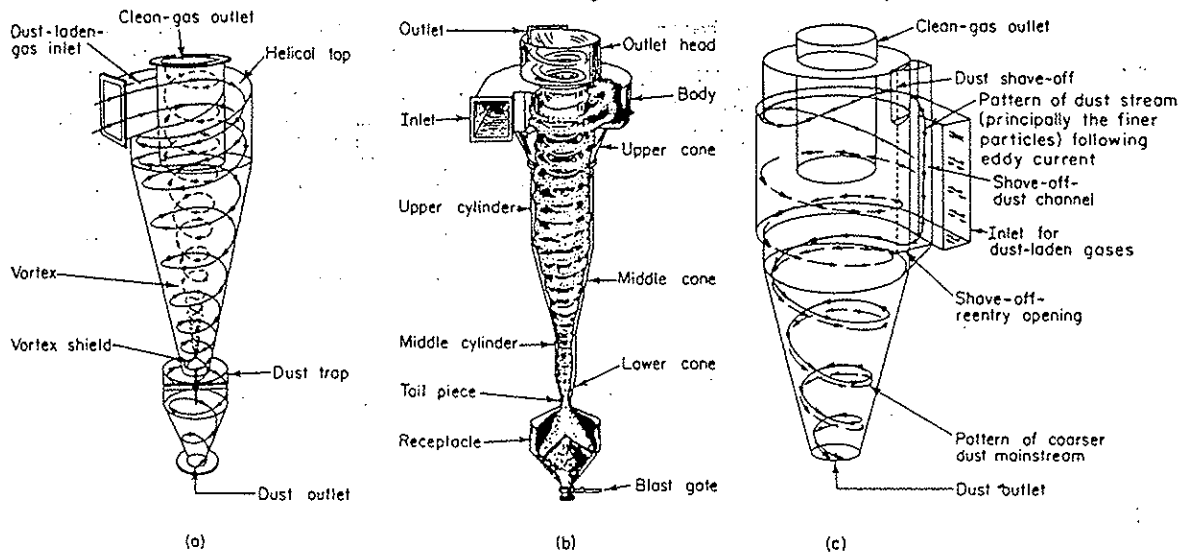


Fig. 13: Direct solar coal gasifier in molten transparent phase.

Duclone collector Sirocco type D Van Tongeren cyclone



20-84 SOLIDS DRYING AND GAS-SOLID SYSTEMS

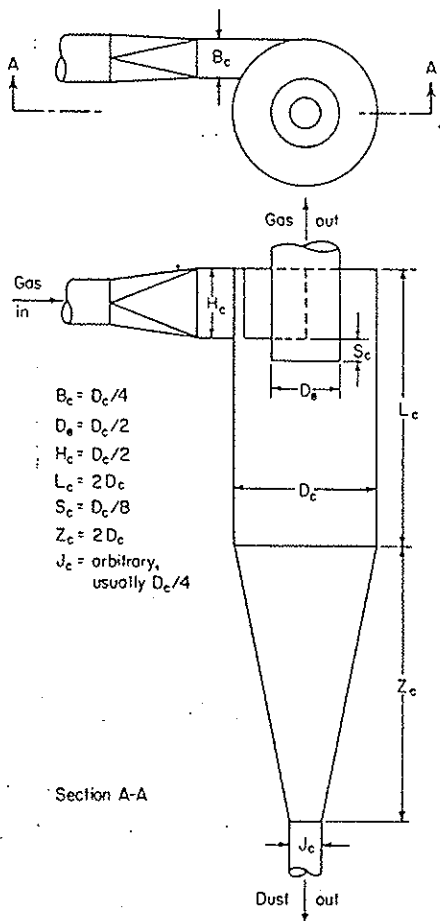


FIG. 20-106 Cyclone-separator proportions.

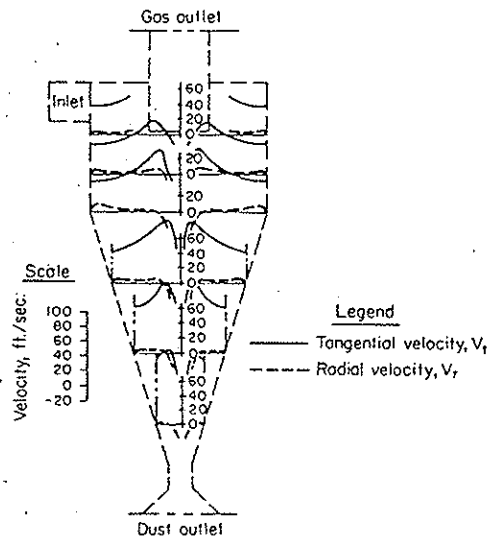


FIG. 20-107 Variation of tangential velocity and radial velocity at different points in a cyclone. [Ter Linden, Inst. Mech. Eng., 160, 235 (1949).]

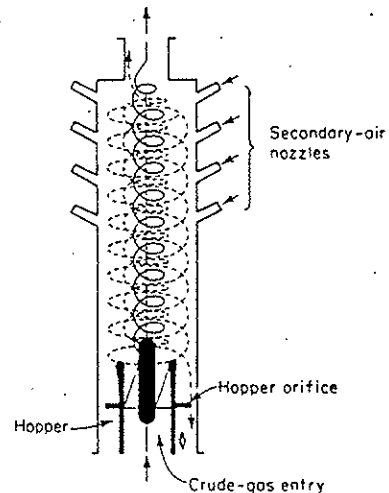


FIG. 20-112 Rotary-flow cyclone. [Teske, Staub, English ed., 30, 35 (1970).]

Fig.14: Different types of cyclone separators.

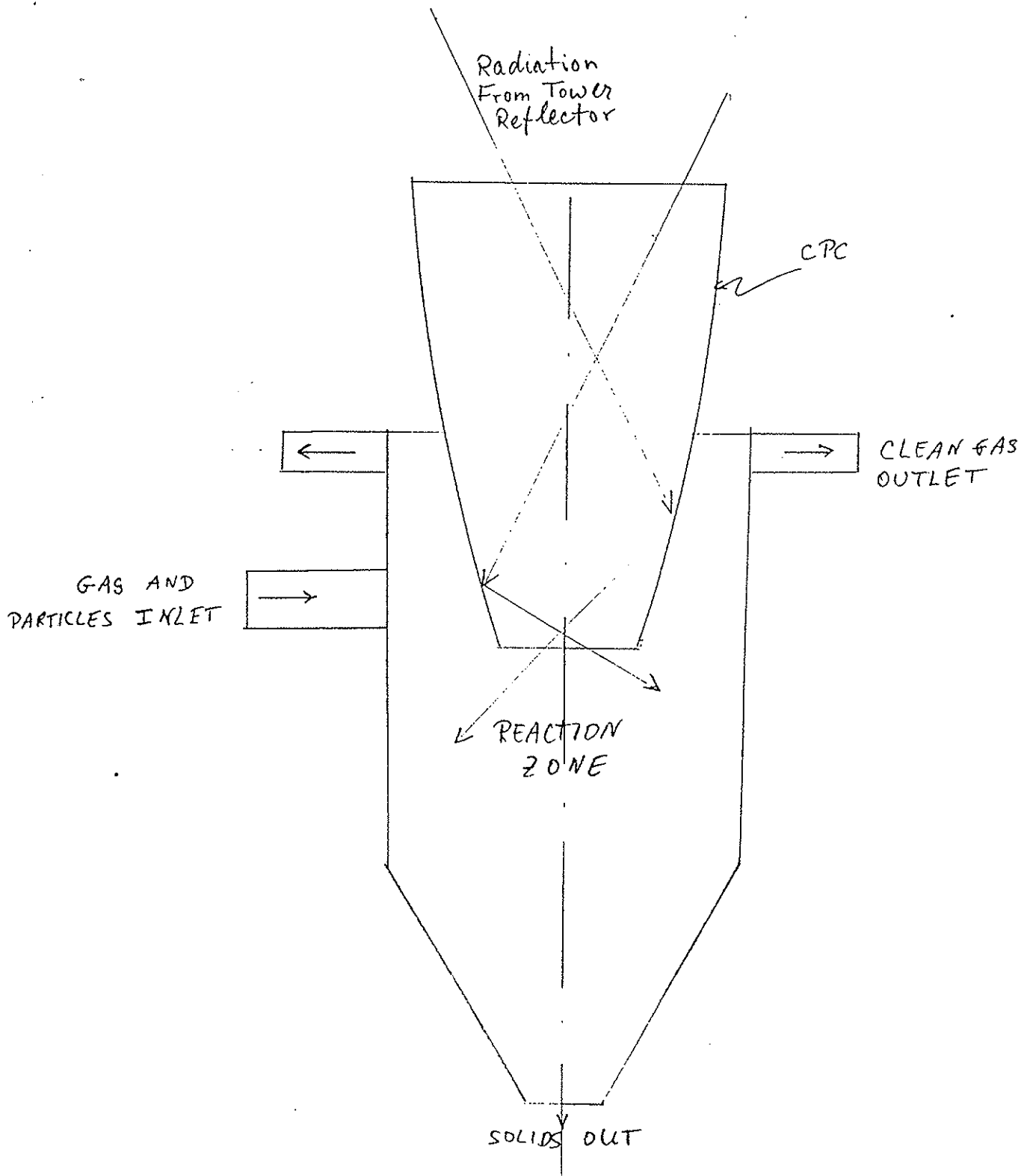


Fig. 15: A scheme of cyclone solar particles reactor equipped with top CPC.

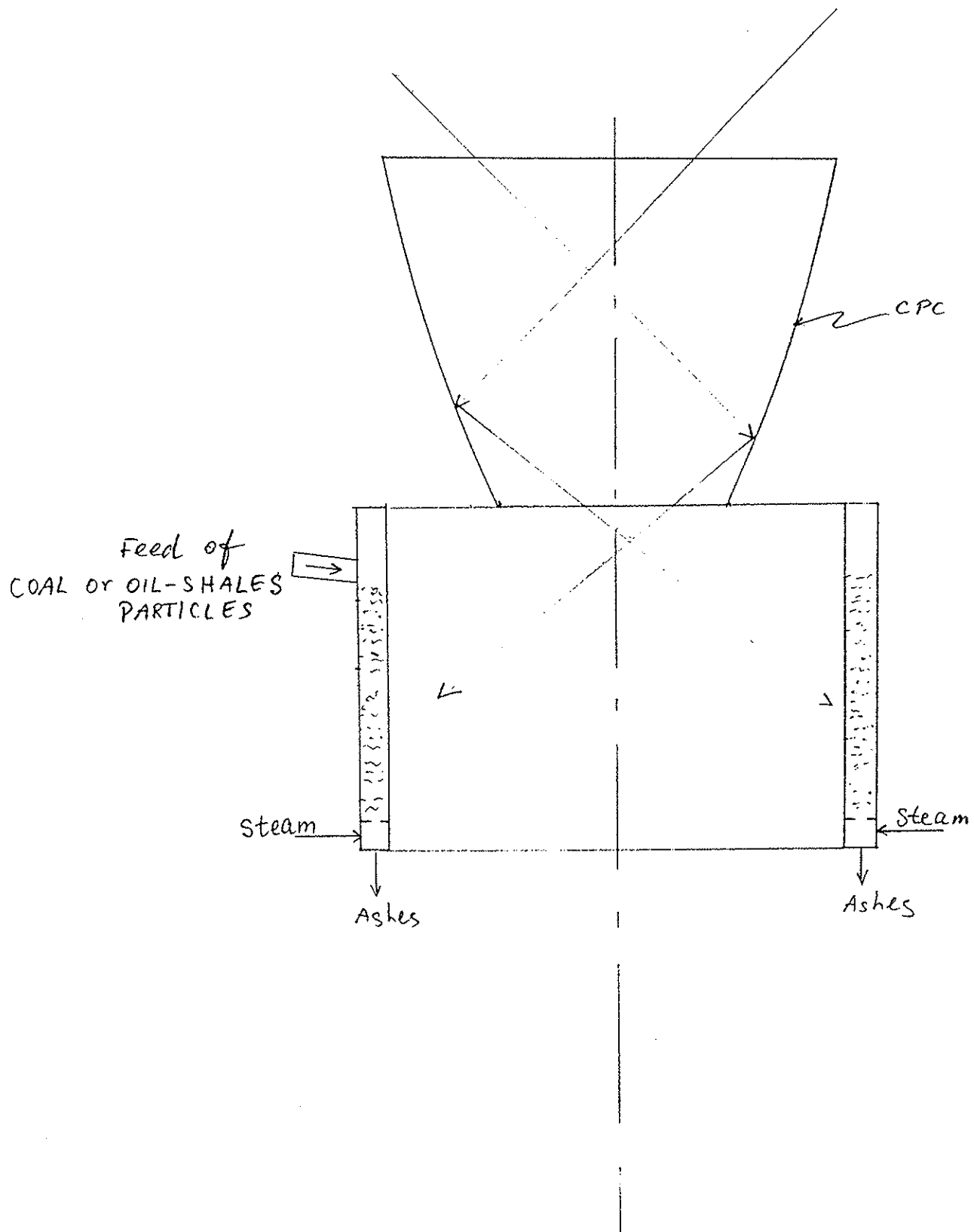


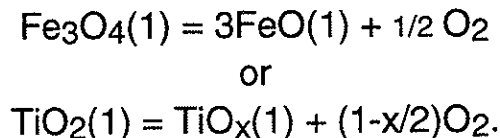
Fig. 16: Annular fluidized bed reactor with solar heating.

The Use of Metal Oxides in High-Temperature Solar Processing

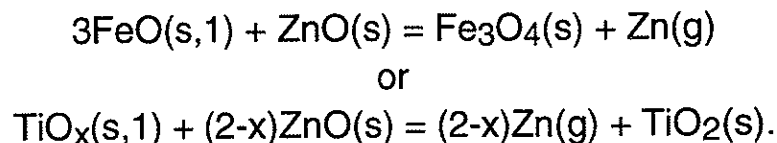
Robert D. Palumbo
Mechanical Engineering Department
Valparaiso University
Valparaiso, IN 46383
USA

A. Rouanet and G. Pichelin
Institut de Science et de Génie des Matériaux et Procédés,
B.P. 5 Odeillo
66120, Font Romeu
France

The products from the thermal decomposition of either Fe_3O_4 or TiO_2 can be used to produce Zn in a two-step high temperature solar thermochemical process. The first step in the processes is a decomposition reaction:



The second step is the reaction of the reduced metal oxides with ZnO to produce Zn:



As the iron and titanium oxides decompose above 2100 K, they experience liquid phase vaporization, O_2 desorption, and O_2 dissociation. The relative importance of each of these phenomenon is governed by the gas phase mass transfer of the molecules from the liquid/gas interface. These decomposition steps can be modeled numerically by coupling the equations of chemical equilibrium to those of steady-state mass transfer. Furthermore, the model helps define, in part, the maximum thermal efficien-

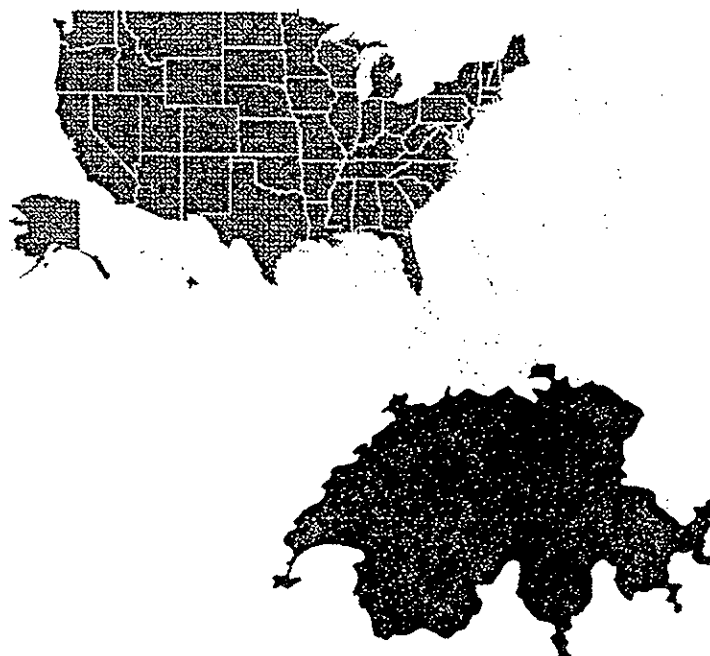
cies of the two-step process: As the extent of decomposition increases, the amount of Zn that can be produced increases, but at the same time greater vaporization and O₂ dissociation occur which tend to decrease process efficiency. We demonstrate that the model is an important tool for optimizing process operating variables.

*THE USE OF METAL OXIDES
IN HIGH TEMPERATURE
SOLAR PROCESSING*

Robert Palumbo

**Mechanical Engineering Department
Valparaíso University
U.S.A.**

**For the International Workshop on
High-temperature Solar Chemistry at the
Paul Scherrer Institute
Switzerland
August 1995**



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(FULBRIGHT COMMITTEE FOR FRANCE)
2. THE CATERPILLAR FOUNDATION
3. VALPARAISO UNIVERSITY

THE WORK WAS CONDUCTED WITH

JARETT MILLAR - VALPARAISO UNIVERSITY

AND

ALAIN ROUANET AND GEORGE PICHELIN

CNRS SOLAR ENERGY LABORATORY

ODEILLO, FRANCE

WE ALSO THANK P.S.I. FOR ENABLING US TO BE HERE.

THE THERMODYNAMICS FOR THE DECOMPOSITION OF TiO_2

GAS PHASE: TiO , TiO_2 , O_2 , O

AND Ar

PROPERTIES TAKEN FROM
JANAF

LIQUID PHASE: TiO_2 Ti_4O_7 Ti_3O_5
 Ti_2O_3 AND TiO

PROPERTIES TAKEN FROM
JANAF

$$G_{\text{MIX}} (\text{LIQUID}) = \sum N_i \times (\Delta G_{\text{FI}}^0 + R \times T \times \ln (X_i))$$

THE THERMODYNAMICS FOR THE
DECOMPOSITION OF Fe_3O_4

GAS PHASE: Fe , FeO , O_2 , O , AND Ar

LIQUID PHASE: FeO Fe_3O_4

PROPERTIES TAKEN FROM JANAF

OR

THERMOCHEMICAL PROPERTIES OF
INORGANIC SUBSTANCES

BY

KNACKE ET AL.

$$G_{\text{MIX}} (\text{LIQUID}) = \sum N_{\text{I}} \times (\Delta G_{\text{FI}}^0 + R \times T \times \text{LN} (X_{\text{I}}))$$

GIBBS PHASE RULE:

$$F = C + 2 - P$$

$$C = 3$$

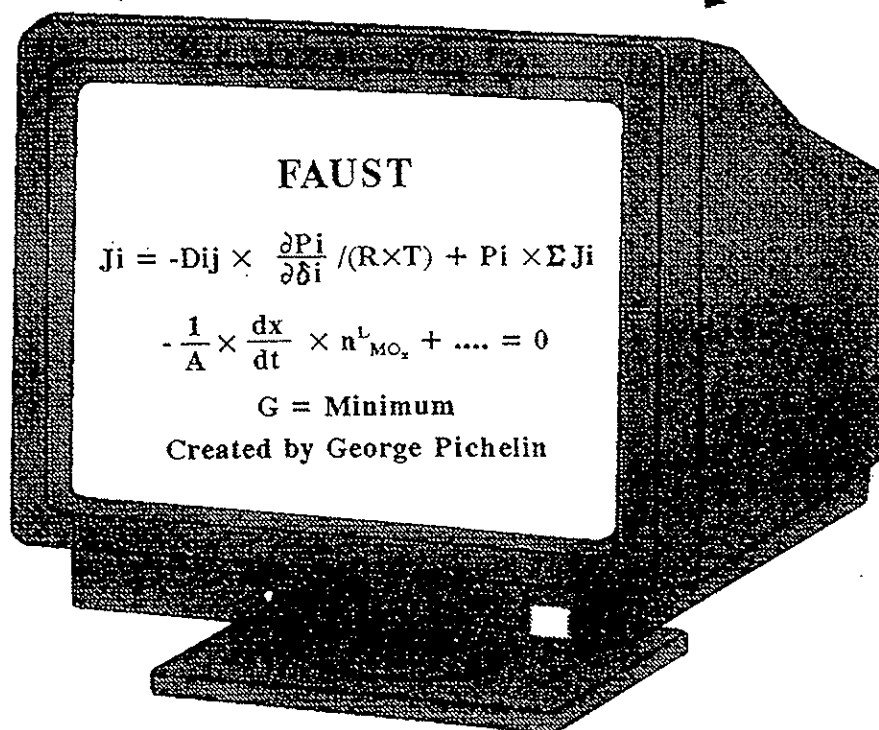
$$P = 2$$

$\therefore F = 3$ AND WE SELECTED P_{TOT} , T , P_{O_2}

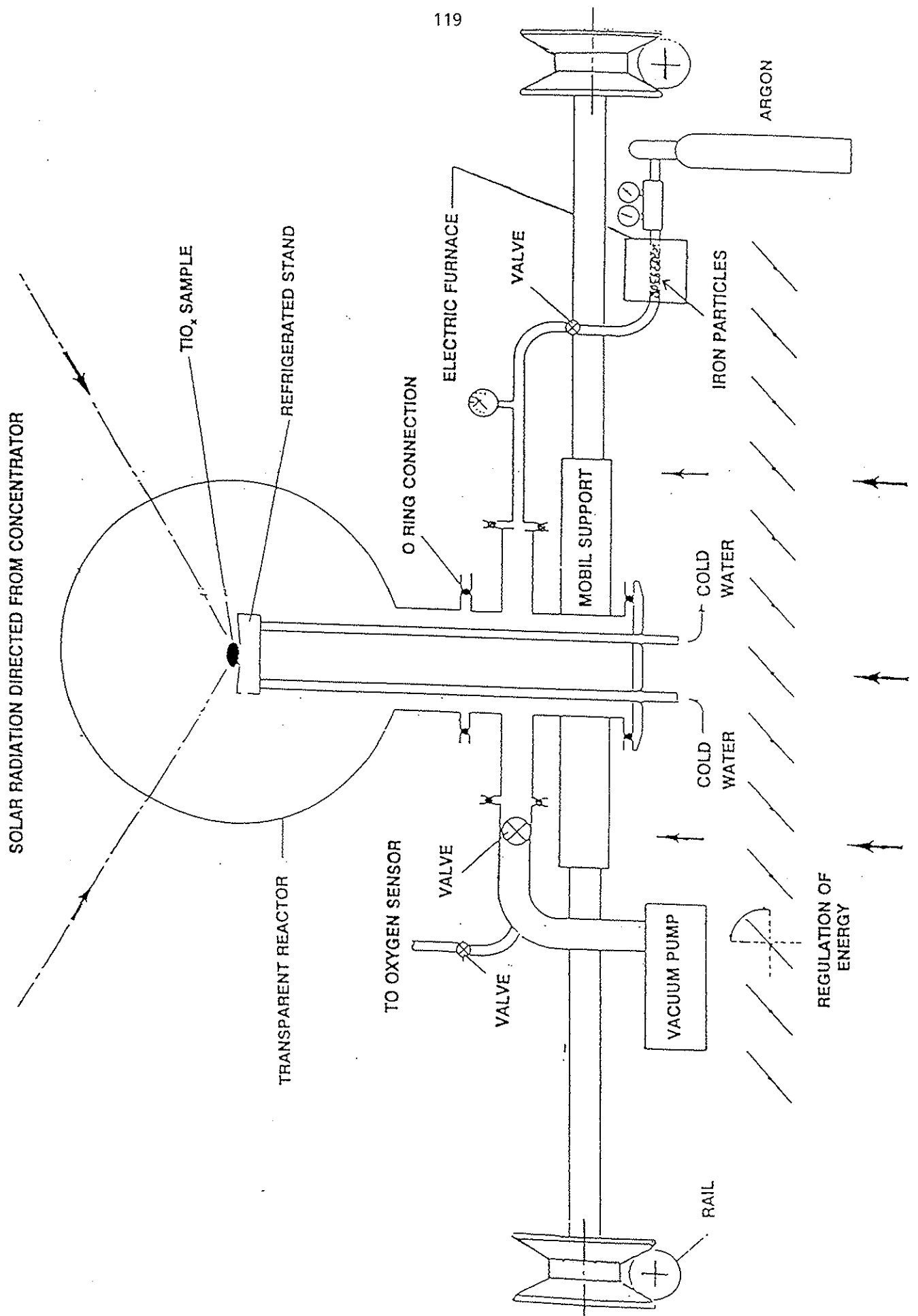
GIBBS FUNCTIONS
Liquid and Gas Phase

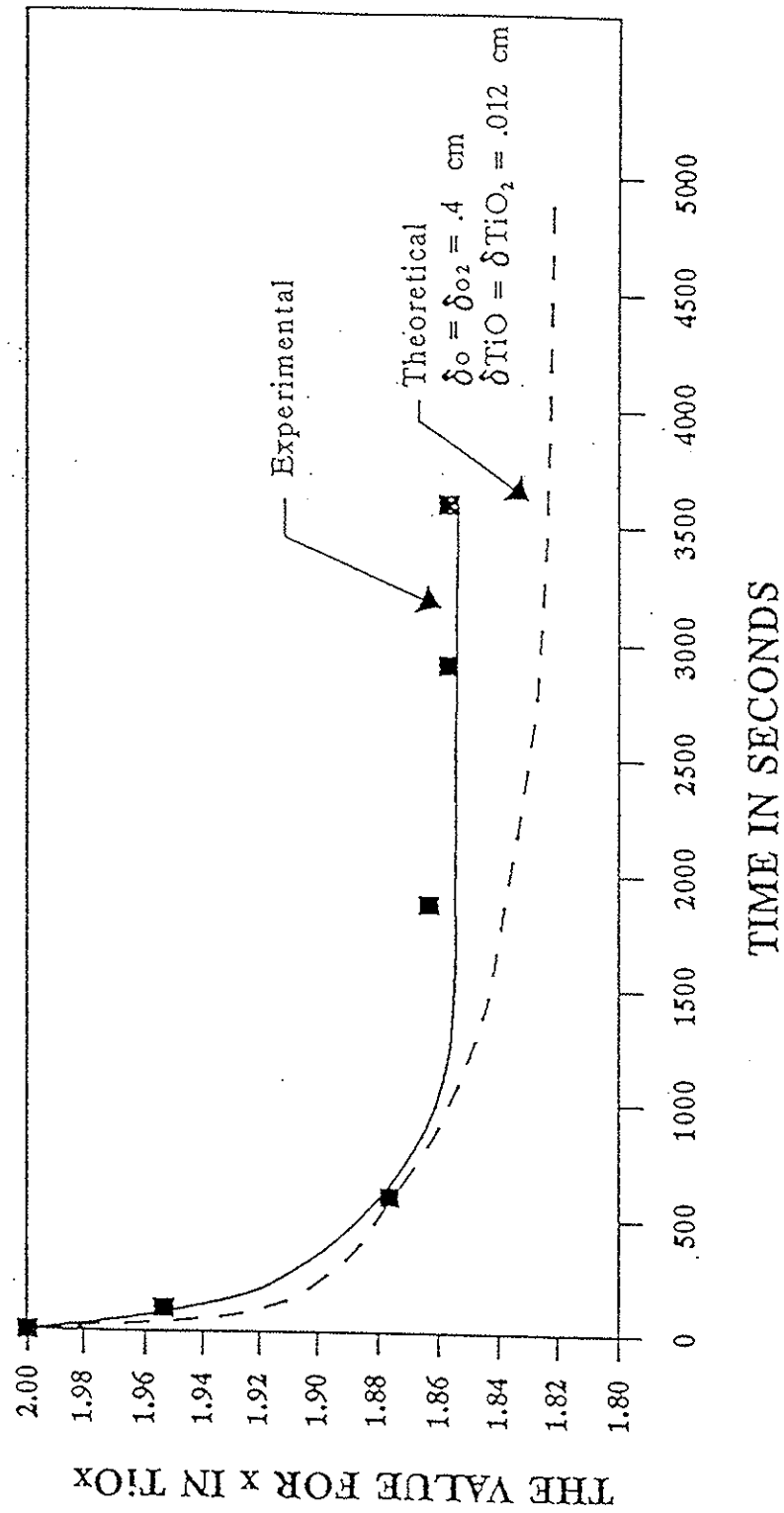
**TRANSPORT
PROPERTIES**

$D_{i,j}$
 δi



time	X	mass loss
t_1	x_1	
t_2	x_2	
t_3	x_3	
	x_4	





Tau During Decomposition of Fe304 at 2200K in AR

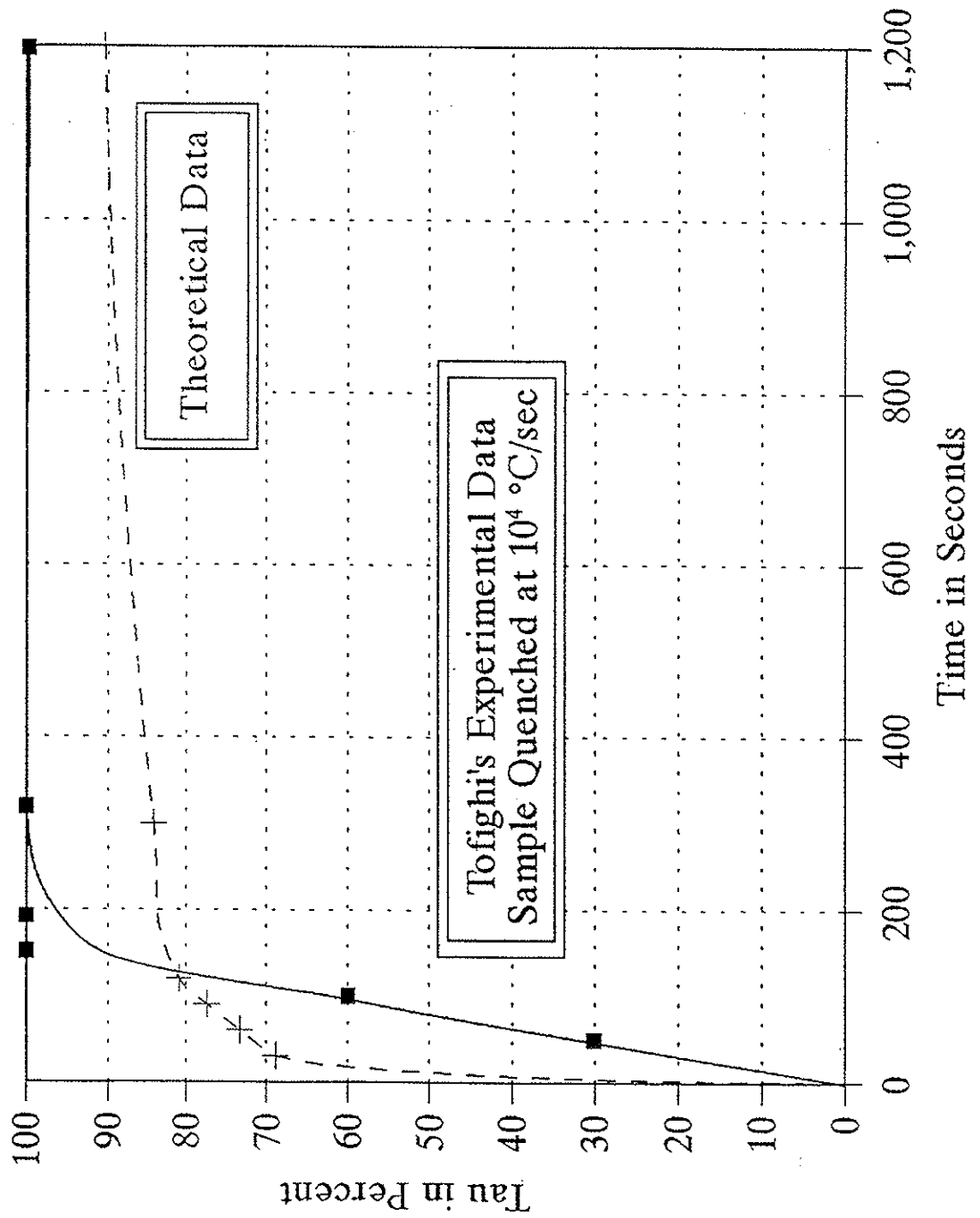
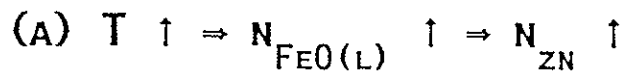


Table 2. Reduction of the condensed mass of a 0.0025 mole sample of TiO_x .

TEMP. (K)	TIME	% REDUCTION, EXPERIMENTAL	% REDUCTION, THEORETICAL
2700	29 min.	10	7.1
2500	37 min.	4.7	3.0
2300	75 min.	1.1	2.3

SOME PARAMETERS THAT AFFECT CYCLE EFFICIENCY

1. GOVERNS NATURE OF PRODUCTS



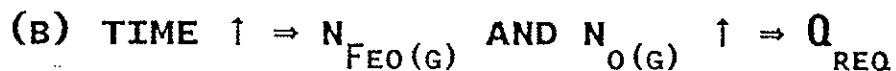
2. GOVERNS REFORMER TEMPERATURE AND $T_{\text{REF}} \uparrow \Rightarrow N_{\text{ZN}} \downarrow$

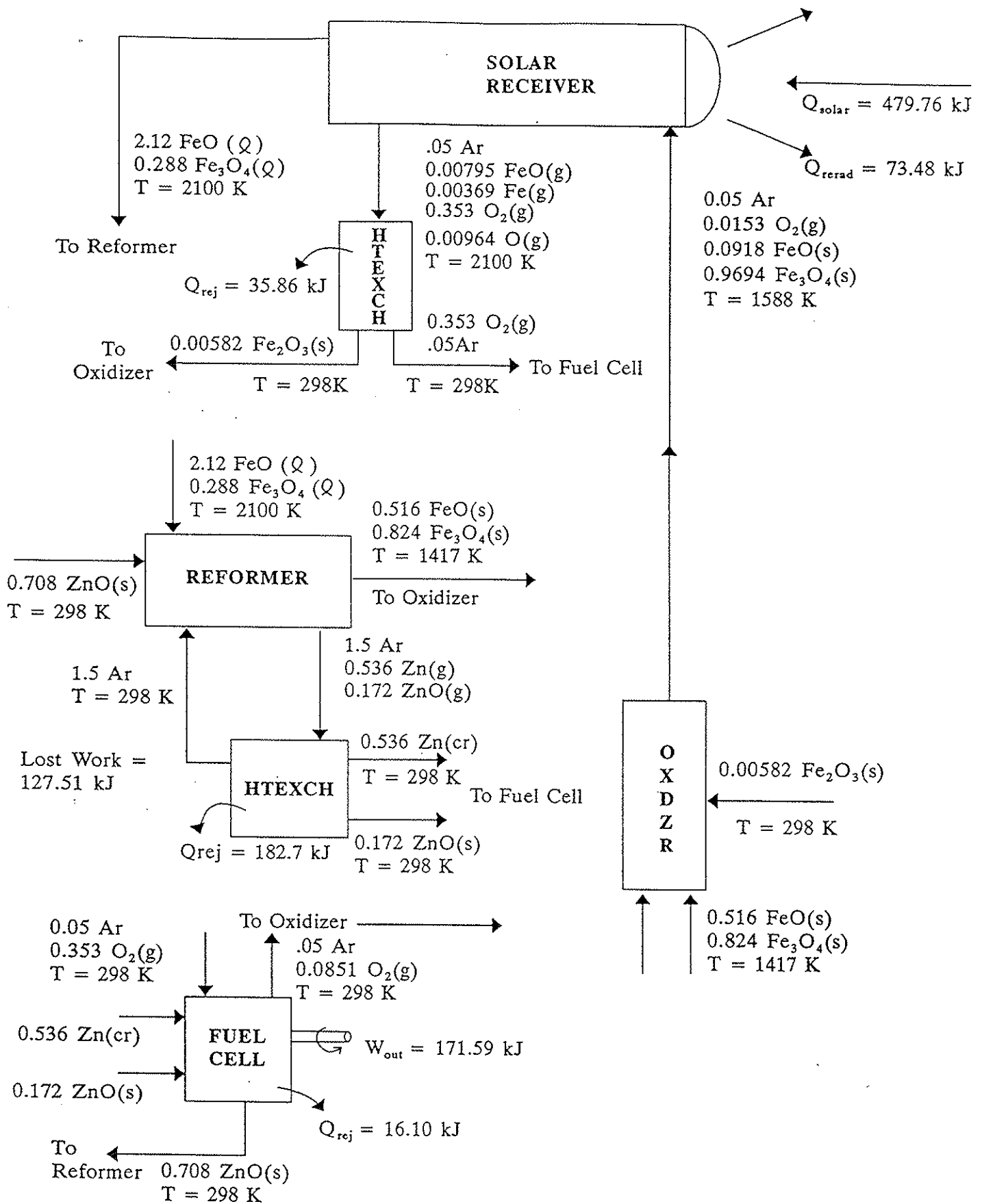
3. GOVERNS RADIATION LOSS

$$T \uparrow \Rightarrow Q_{\text{LOSS}} \uparrow$$

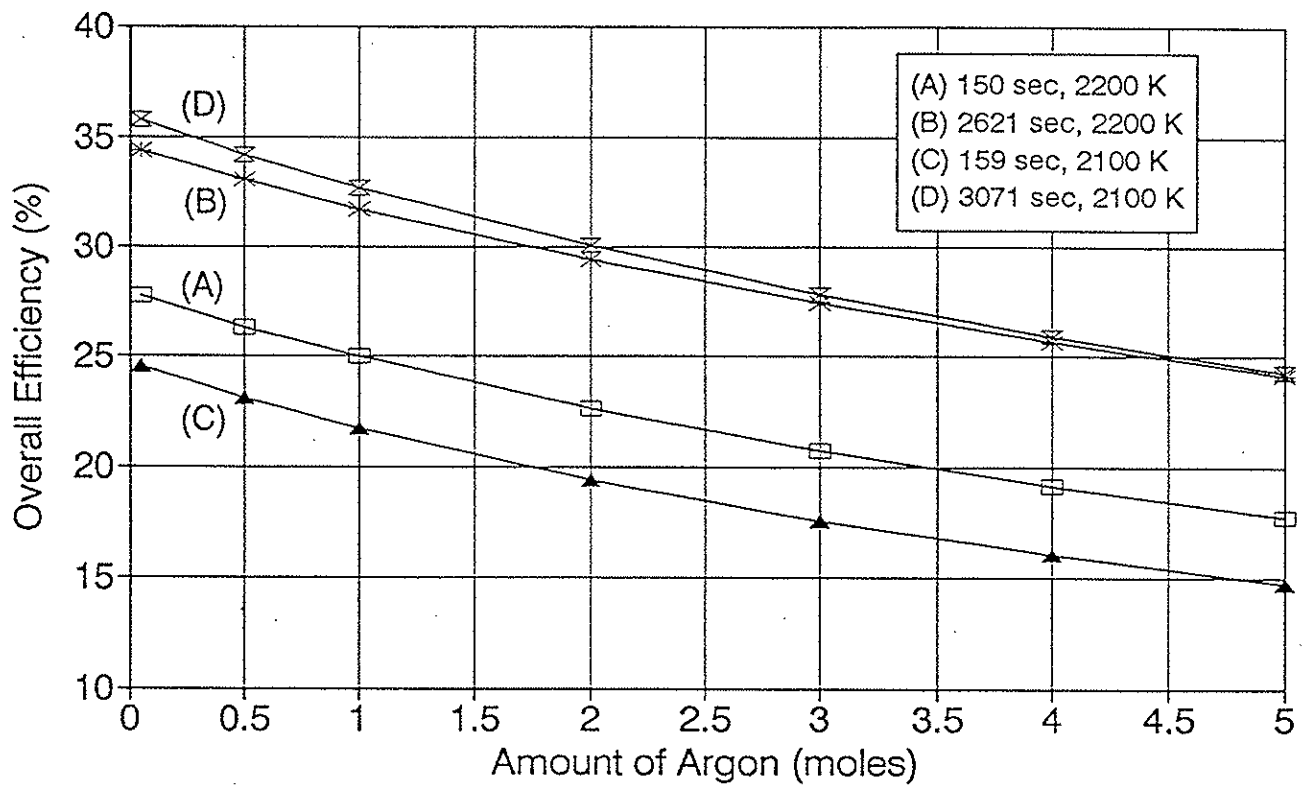
RESIDENT TIME IN SOLAR RECEIVER

1. GOVERNS NATURE OF PRODUCTS





Cycle Efficiency vs Quantity of Ar Heated to Receiver Temperature



Solar-Assisted Chemical Processes - A Way Out of the Fossil Energy Systems?

Armin Reller*)
Inorganic and Applied Chemistry Institute
University of Hamburg
Martin-Luther-King-Platz 6
D-20146 Hamburg
Germany

At present 90% of the world energy consumption is covered by fossil fuels. The consumers and the spectrum of what the energy is used for reveal to be extremely polarized into regionally different scenarios [1]. There is no doubt that the substitution of fossil energy systems by regenerative energy systems, i.e. by using "direct" or "indirect" solar energy in industrial processes, will be a stepwise development. Therefore, optimal implementation strategies for a timely and sustainable substitution are decisive. Boundary conditions with respect to the required resources, processes as well as regional necessities of life have to be chosen such that first steps of solar or regenerative energy substitution can be realized. Examples of successful activities are photovoltaic power plants as example of converting "direct", i.e. solar radiation energy, or wind farms as example of converting "indirect" solar energy. Here projects are presented where high temperature solar processes are used for different purposes:

- High temperature process heat is obtained in advanced volumetric absorber systems (temperature of heat transport medium: $> 750^{\circ}\text{C}$). Regarding actual developments of ever growing large agglomerations, i.e. so-called megatowns, potential applications in the urgently needed cement production are discussed.

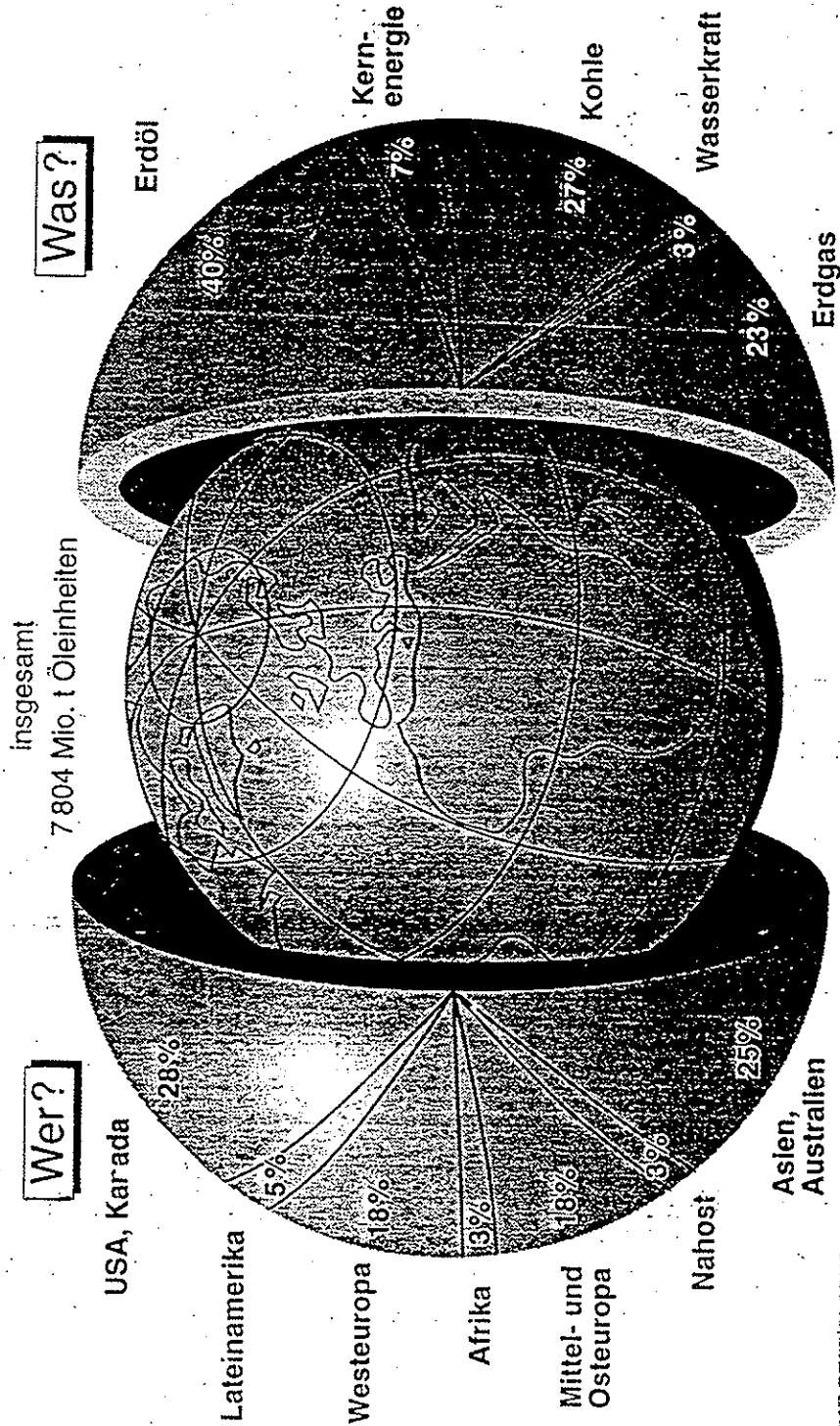
*) *In collaboration with P. Kuhn, A. Steinfeld, K. Ehrensberger, O. Becker, U. Sazama, M. Pyrkänen, M. Posnansky, A. Imhof and H. Fricker.*

- Solar-driven production of hydrogen peroxide and hydrogen by splitting water using reversible processes in metal oxides as process mediators. Hydrogen peroxide is a very important basic compound for the purification and detoxification of fresh water, hydrogen most probably one of the most important energy carriers and certainly one of the most important future reducing agents in industrial processes [2].
- Solar assisted production of metals from metal ores such as oxides, carbonates, silicates and sulfides. This option is demonstrated by studies on e.g. the production of iron from iron oxide ores, nickel from nickel silicates, zinc from zinc silicates as well as copper and iron from chalcopyrite. As reducing agents hydrogen, methane or natural gas are used. In case of reducing agents containing carbon the simultaneous formation of synthesis gas is emphasized.

The integration of these processes and its products in energy and process networks and the implementation into appropriate regions is shortly discussed.

- [1] *Energie und Umwelt*, K. Heinloth, Verlag der Fachvereine, Zürich (1993).
- [2] See also: H.R. Oswald, lecture on this *IEA-Solar PACES International Workshop* (1995).

Welt-Energieverbrauch 1993



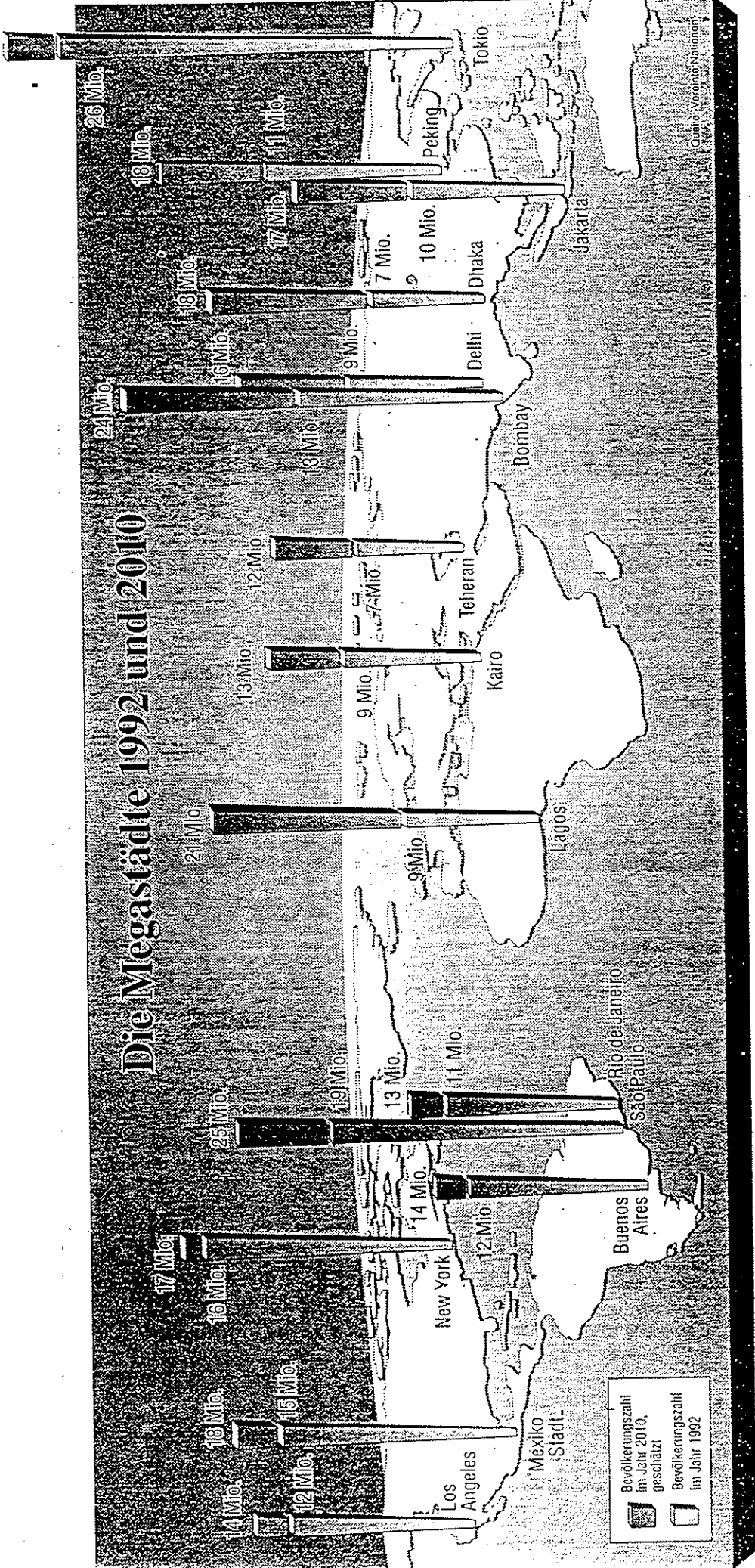
Unmäßig

Ungleich der Energieverbrauch auf dem Planeten kaum verteilt sein: Nur etwas mehr als zehn Prozent der Weltbevölkerung, Nordamerikaner und Westeuropäer, verbrauchen fast die Hälfte jenes Stoffes, der zu Luxus und Wohlstand verhilft. Asien dagegen begnügt sich mit weniger als einem Viertel des Weltenergieverbrauchs, obwohl allein in China mehr als zwanzig Prozent der Menschheit lebt. Würden freilich alle Menschen soviel Energie verbrauchen wie die Wohltatsbürger, wäre es um die Zukunft des Planeten schlecht bestellt. Denn zu neunzig Prozent beruht die Energieversorgung auf Erdöl, Kohle und Erdgas, bei deren Verbrennung klimaschädliches Kohlendioxid freigesetzt wird. Der Energieverbrauch müßte deshalb sinken – doch die Prognosen verheßen genau das Gegenteil. Düstere Aussichten.

Quelle: BP

29 Mio.

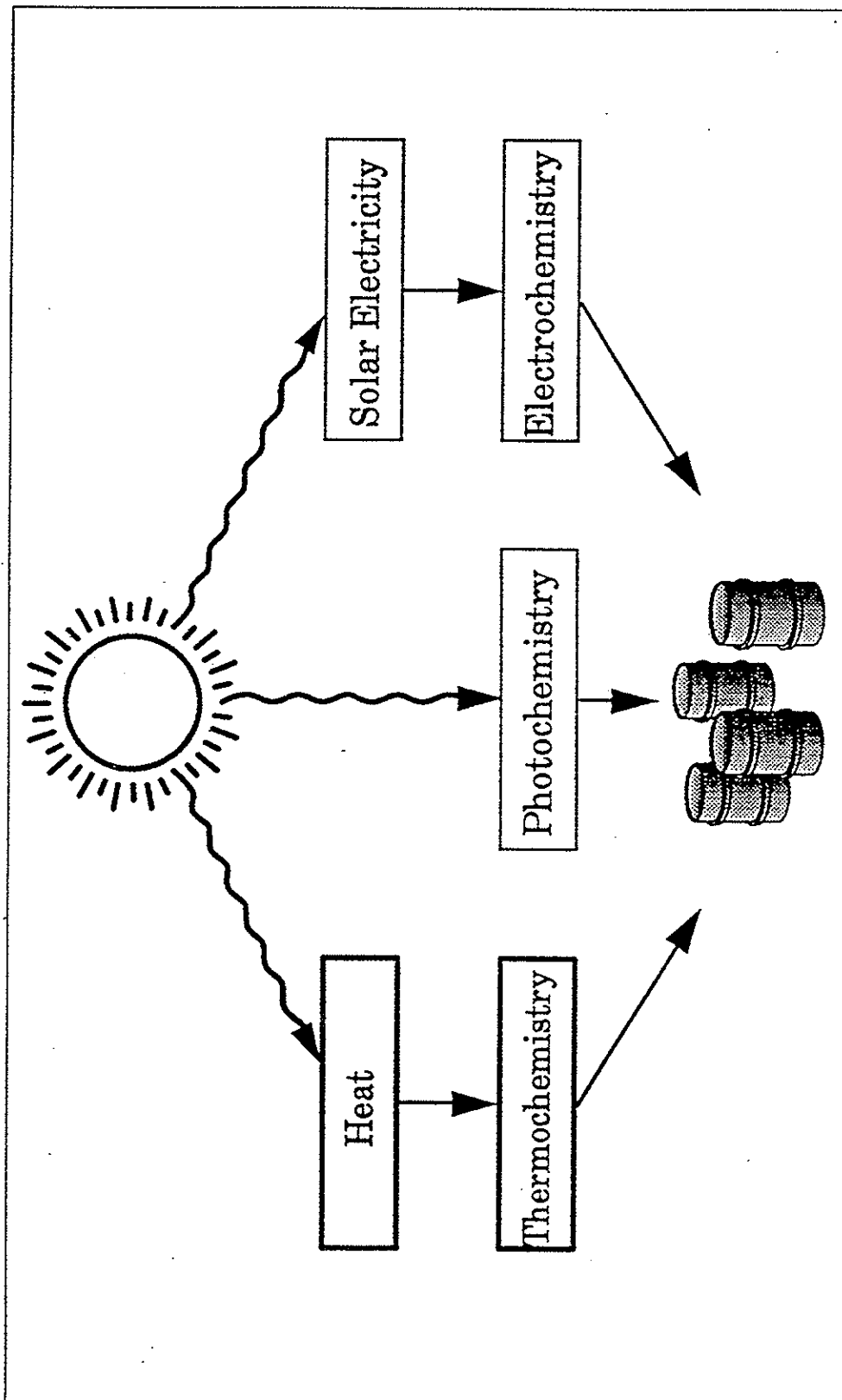
Die Megastädte 1992 und 2010



Bevölkerungszahl im Jahr 2010, geschätzt
Bevölkerungszahl im Jahr 1992

Die 15 Megastädte der Welt und ihr Wachstum, geschätzt von den Vereinten Nationen. Doch die Zahlen müssen von Jahr zu Jahr korrigiert werden

Quelle: Vereinte Nationen 1994



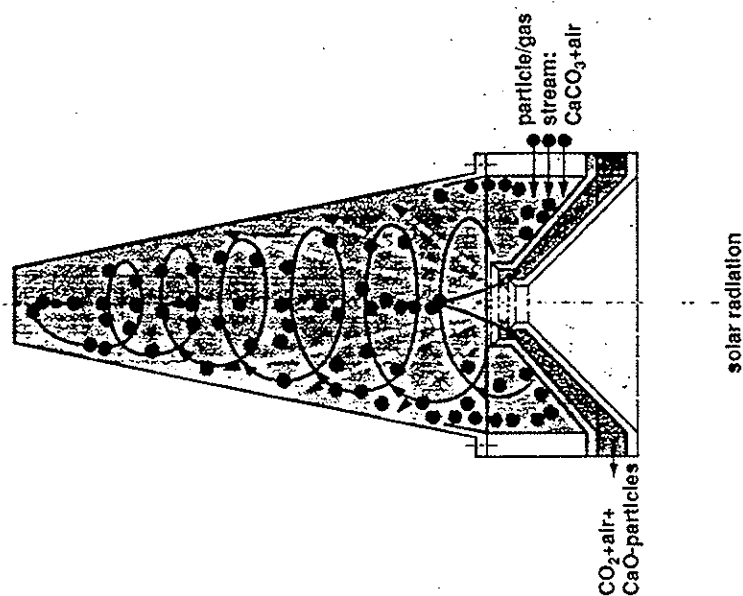
Reaction



Test Conditions

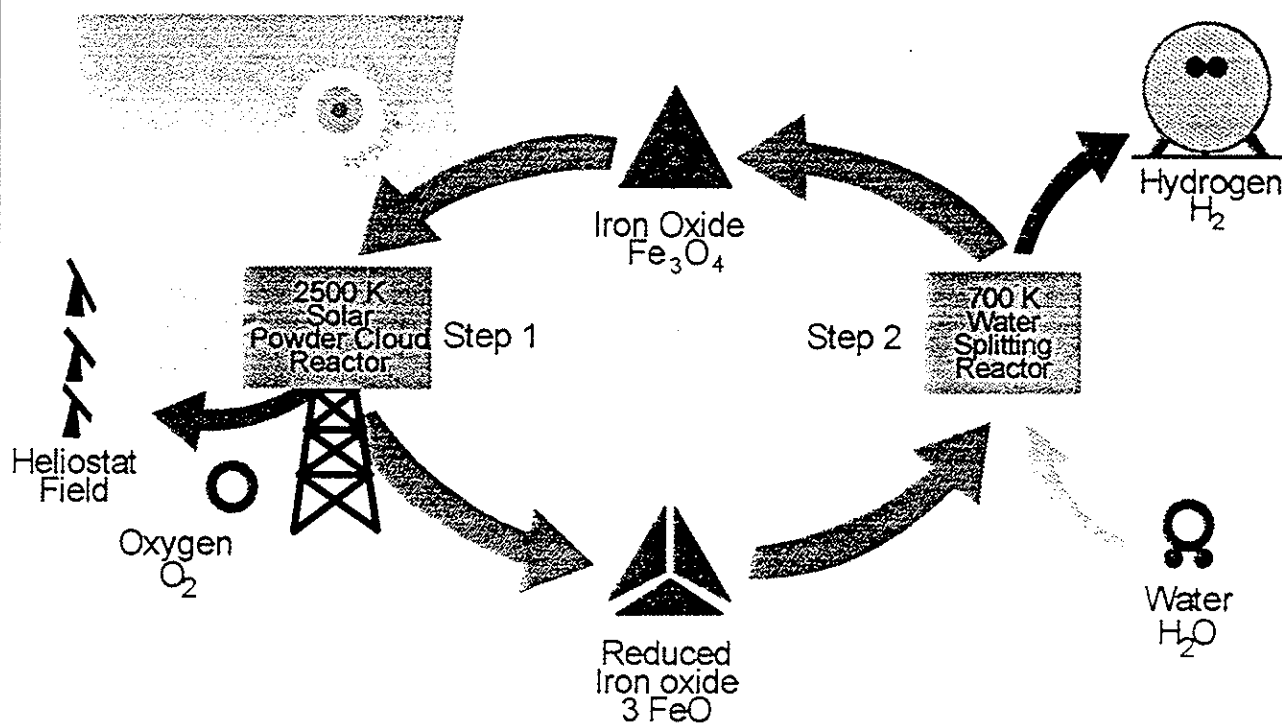
Inlet air flow rate	ca 60 kg/h
Outlet air flow rate	ca 90 kg/h
Reactor mean wall temp.	ca 1200°C
Total incoming power at 850 W/m ²	ca 68 kW
Degree of calcination	40 ÷ 65%

Scheme of Cyclone Reactor



PSI / BUZ - Patent EP 92 105 191.8, A. Imhof

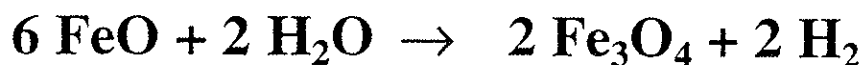
Solar Thermochemical Cycle for Hydrogen Production



Step 1: Solar Thermal Dissociation

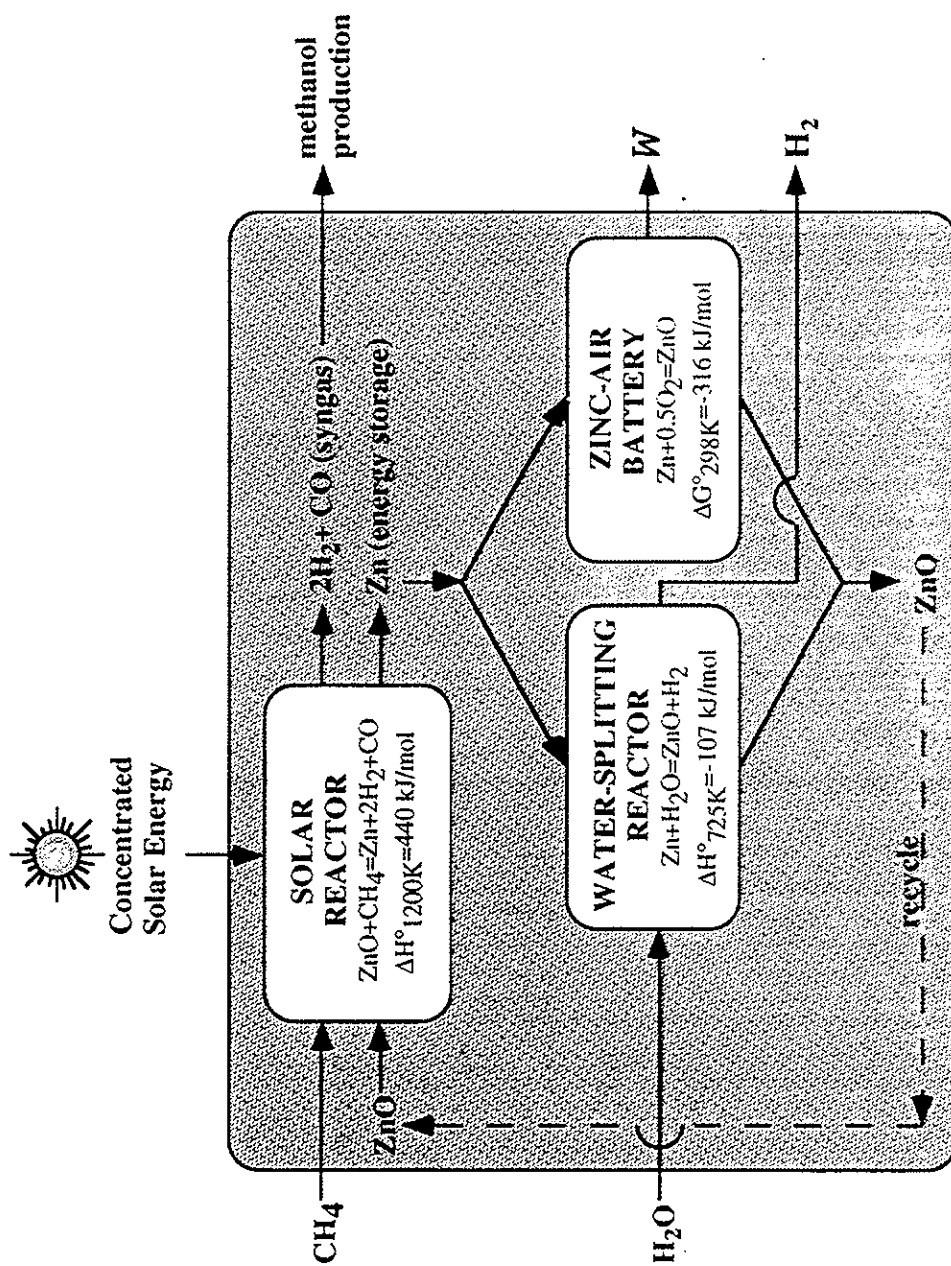


Step 2: Water Splitting



Net Reaction:





Solar Thermal Processes Using Metal Carbides and Nitrides

Jean P. Murray
 Department of Mechanical Engineering
 Portland State University,
 P.O. Box 751
 Portland, OR 97207-0751
 USA

It is hoped that we will begin a transition to an energy economy that is not based on carbon combustion, releasing CO₂ to the atmosphere, but is instead based on hydrogen and hydrogen cycles. Yet there may always be a place for hydrocarbons if their CO₂ emissions can be reduced, especially in the transportation sector. Metals and their oxides have been studied for use in cycles that use high-temperature solar energy to produce hydrogen, or other energy carriers. The feasibility, based on a study of the equilibrium thermodynamics and a literature survey to find the kinetics of the candidate reactions and overall system operation for a similar system based on metallic nitrides or carbides has been investigated. In many cases, it is far easier to form the carbide or nitride than to completely reduce the oxide as required to split water: the temperatures required are lower, and all reactants appear in the solid phase. Furthermore, valuable products such as methane, acetylene, and other hydrocarbons, and ammonia may be formed by hydrolysis reactions with the carbides or nitrides.

The light-metal carbides lithium carbide, Li₂C₂, aluminum carbide, Al₄C₃, cementite Fe₃C, and silicon carbide, SiC, can be used in a cycle based on the carbides to produce H₂ and CO at the solar reactor, and store solar energy that can be recovered as CH₄, C₂H₂ or other hydrocarbons when the carbide is hydrolyzed. At the high-temperature solar reactor, the carbides Li₂C₂, Al₄C₃, Fe₃C or SiC would be made from a reaction between the metallic oxides and either C-a proven technology, or CH₄-still to be fully tested. Each of these carbides reacts with water under various conditions to yield either methane, or higher hydrocarbons like acetylene.

Consider a cycle based on SiC, which illustrates the general scheme but is not the best choice in terms of conditions required for the hydrolysis reactions:

In the Solar Reactor :



The CO can be further shifted to H₂ if desired, or the mixture used in the manufacture of methanol or other chemicals.

Later, at a remote site, in a vehicle, or at the solar facility for greater carbon recycle, the SiC can be hydrolyzed to yield CH₄ and SiO₂:



with complete conversion at 100MPa; 700°C, 12 hours.

A similar reactor could be used to manufacture NH₃ from aluminum nitride. For example, AlN can be made by reaction of alumina (Al₂O₃) and carbon (C) or methane (CH₄) in nitrogen (N₂) at temperatures no higher than 1850K. When hydrolyzed, even at ambient temperatures, the nitride forms NH₃, and the oxide can be recycled. Carbon monoxide released during the nitridation process can be shifted to hydrogen; and even the NH₃ can be split if H₂ is the preferred product.

Li₂C₂ and Al₄C₃ have been proposed as a means of producing fuel for vehicles using coal combustion as both process heat and carbon source; a reaction conducted with solar process heat would release far less CO₂ to the atmosphere.

Carbide and Nitride Processes for Production of Hydrogen, Hydrocarbons and Ammonia

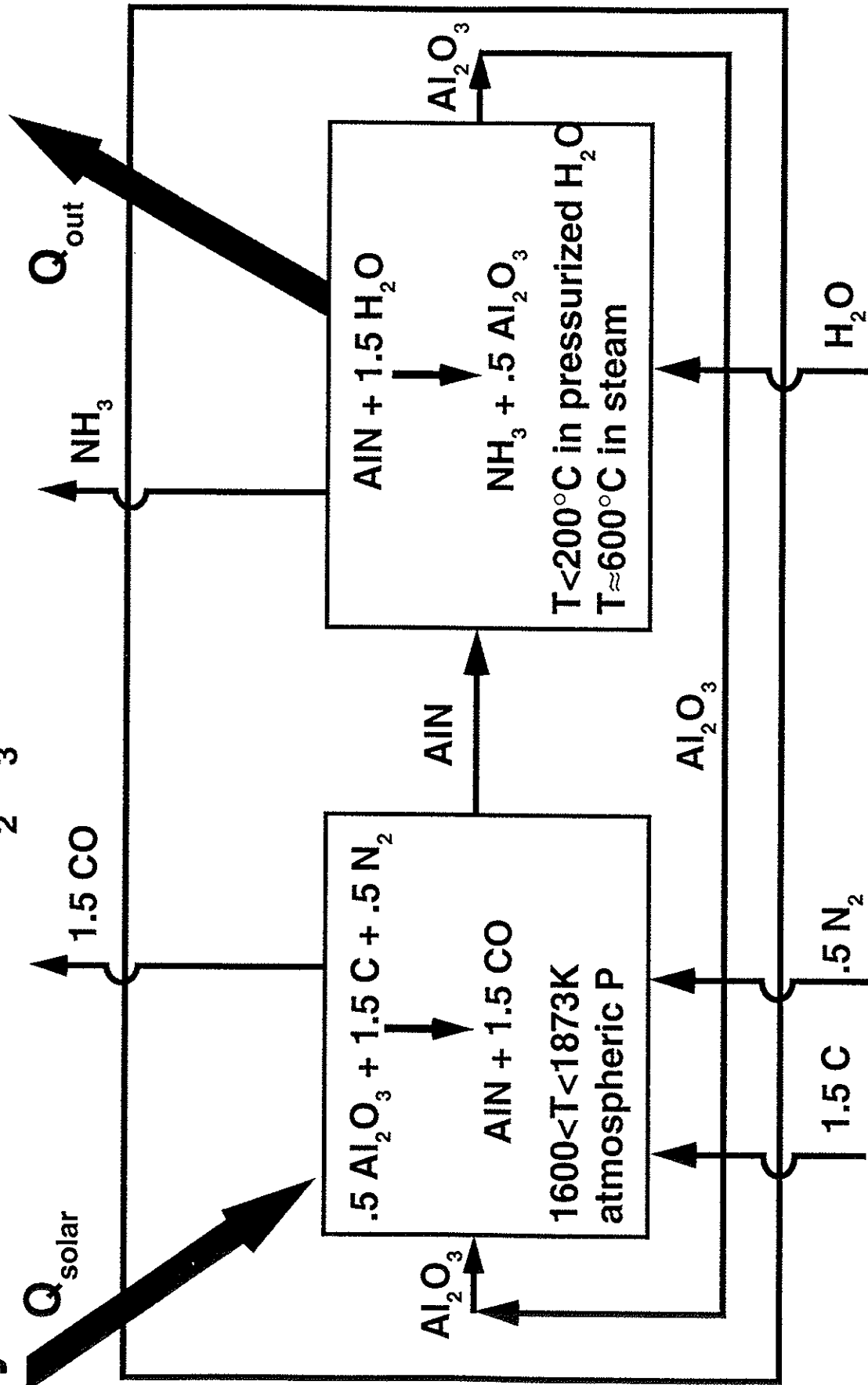
Jean P. Murray

**Department of Mechanical Engineering
Portland State University**

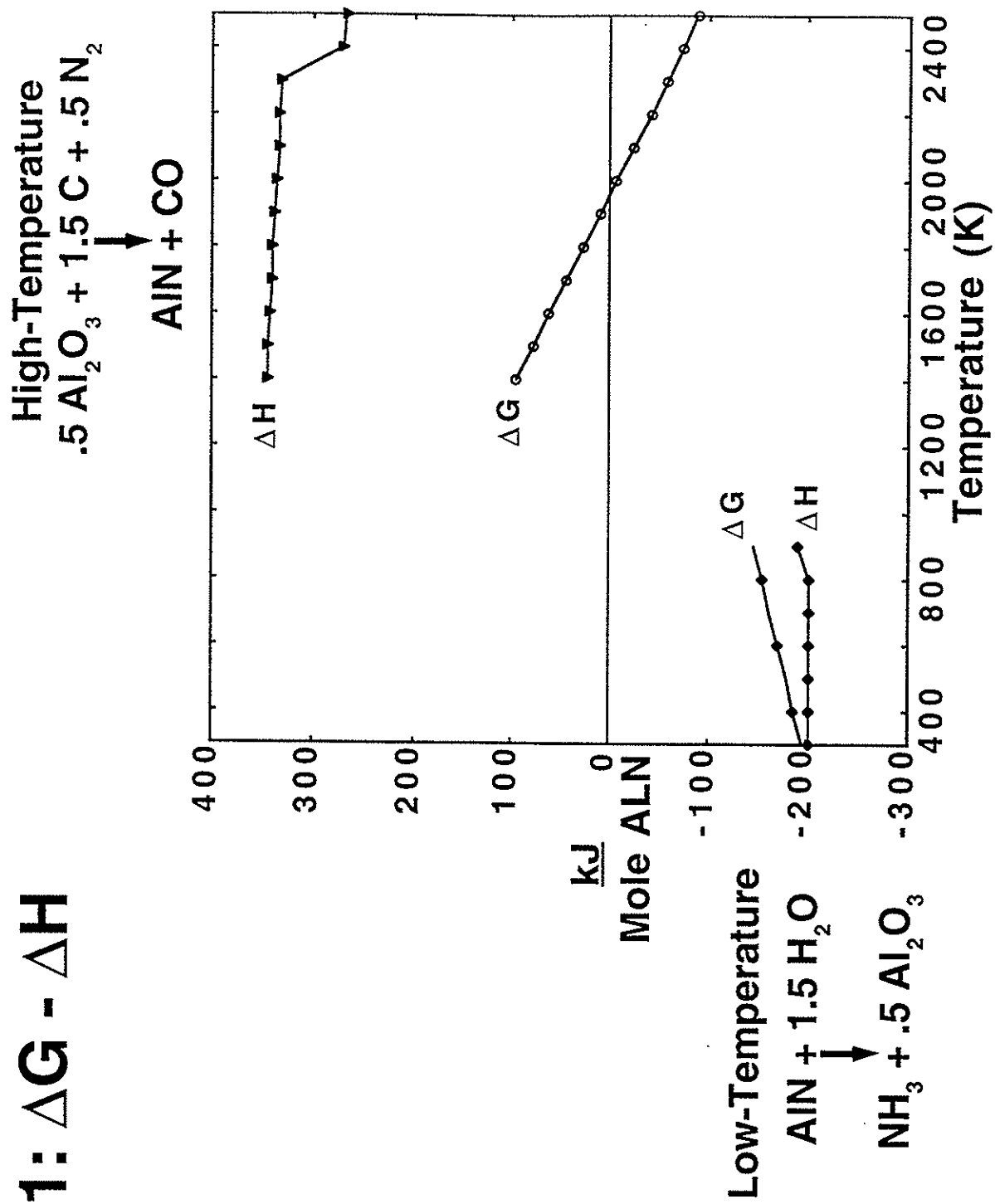
Examination of feasibility of 1 Oxide-Nitride and 5 Oxide-Carbide Cycles

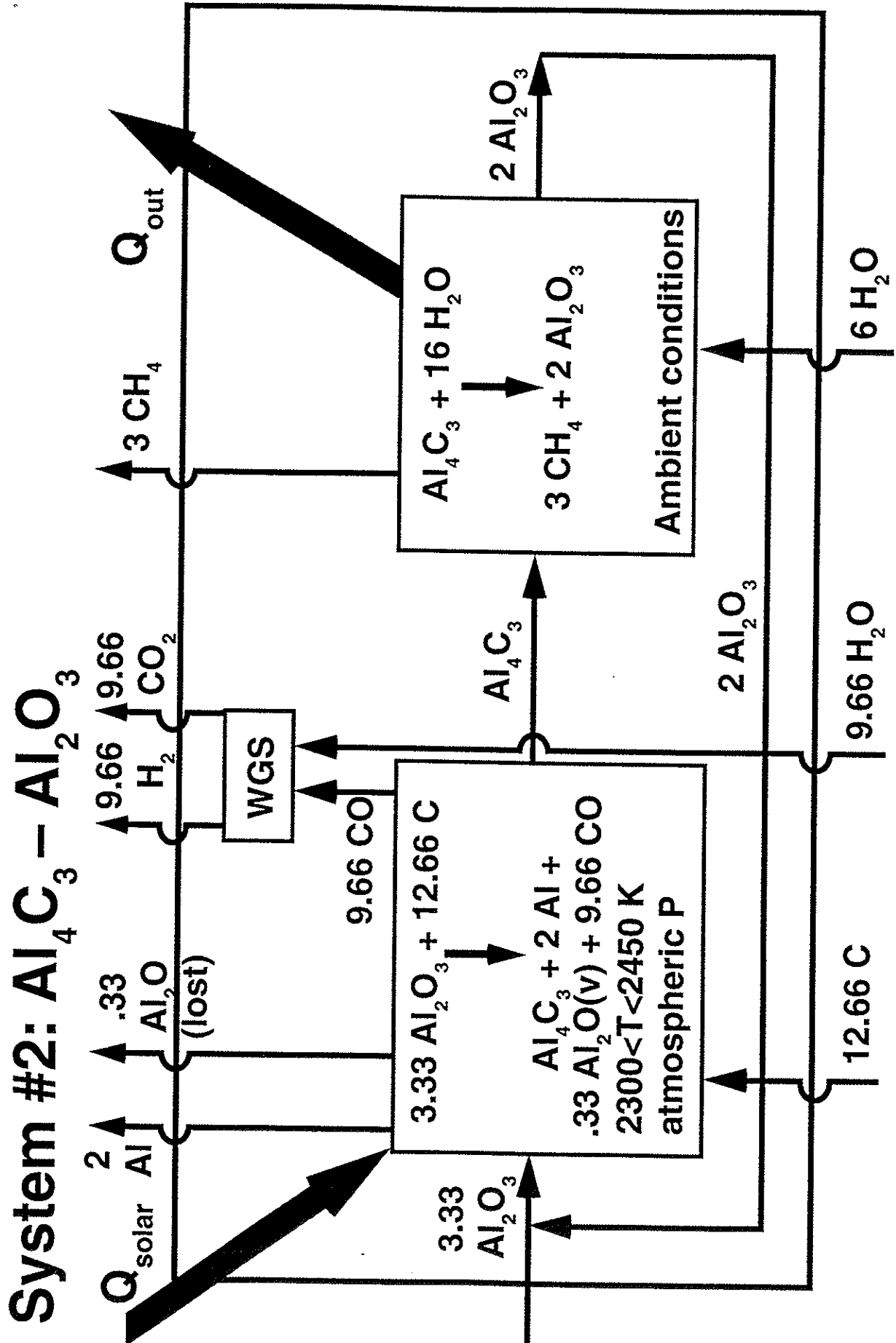
- Cycles of interest :
 - carbothermic at high-temperature
 - return hydrocarbons and H₂ by hydrolysis
- Based on Preliminary Literature Survey and Patent Information
 - Specify Operating Process T, P
 - Specify products in general
- Preliminary calculations for process thermochemistry

System #1: $\text{AlN} - \text{Al}_2\text{O}_3$

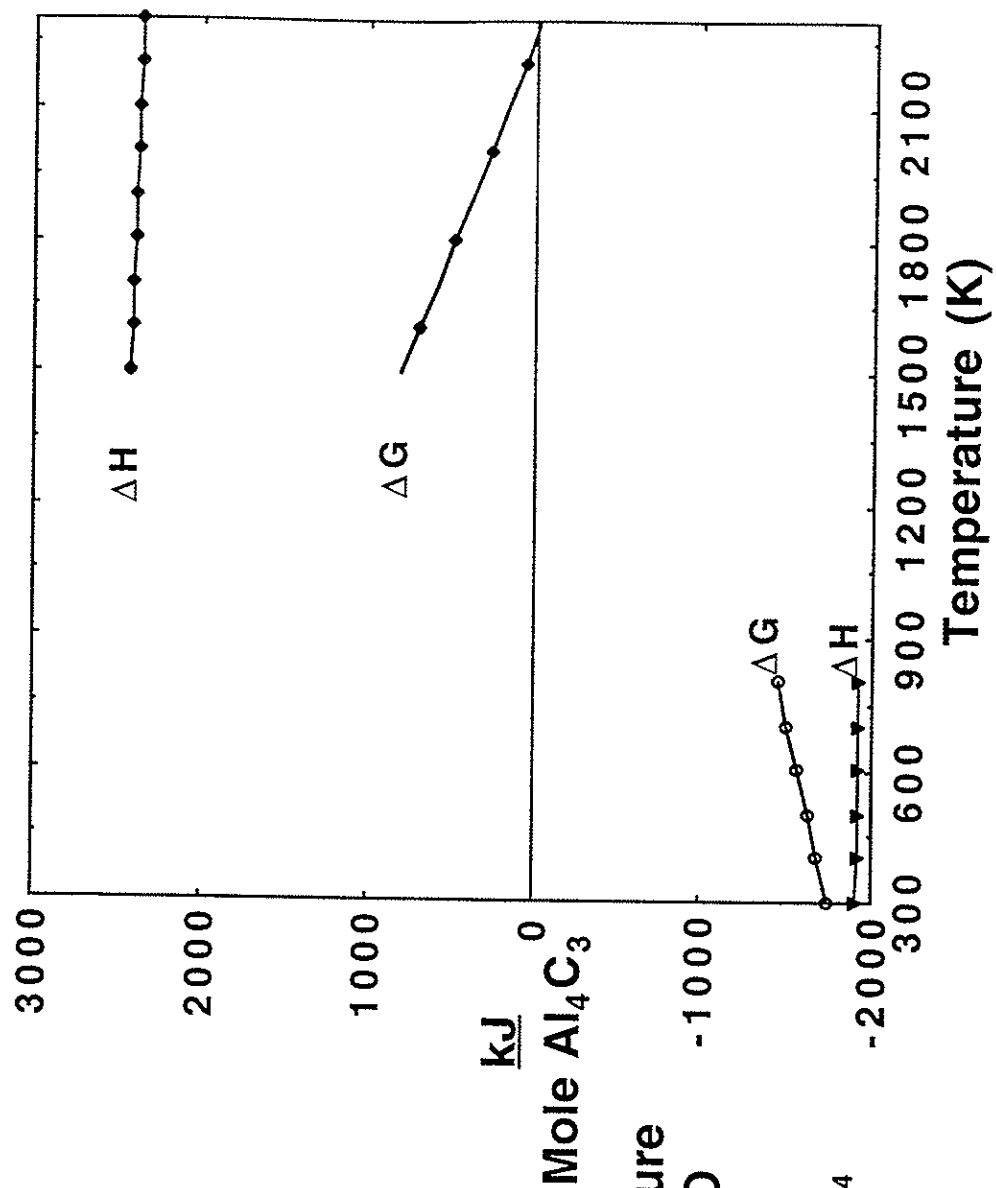
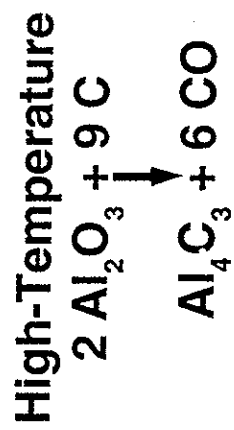


System #1: $\Delta G - \Delta H$

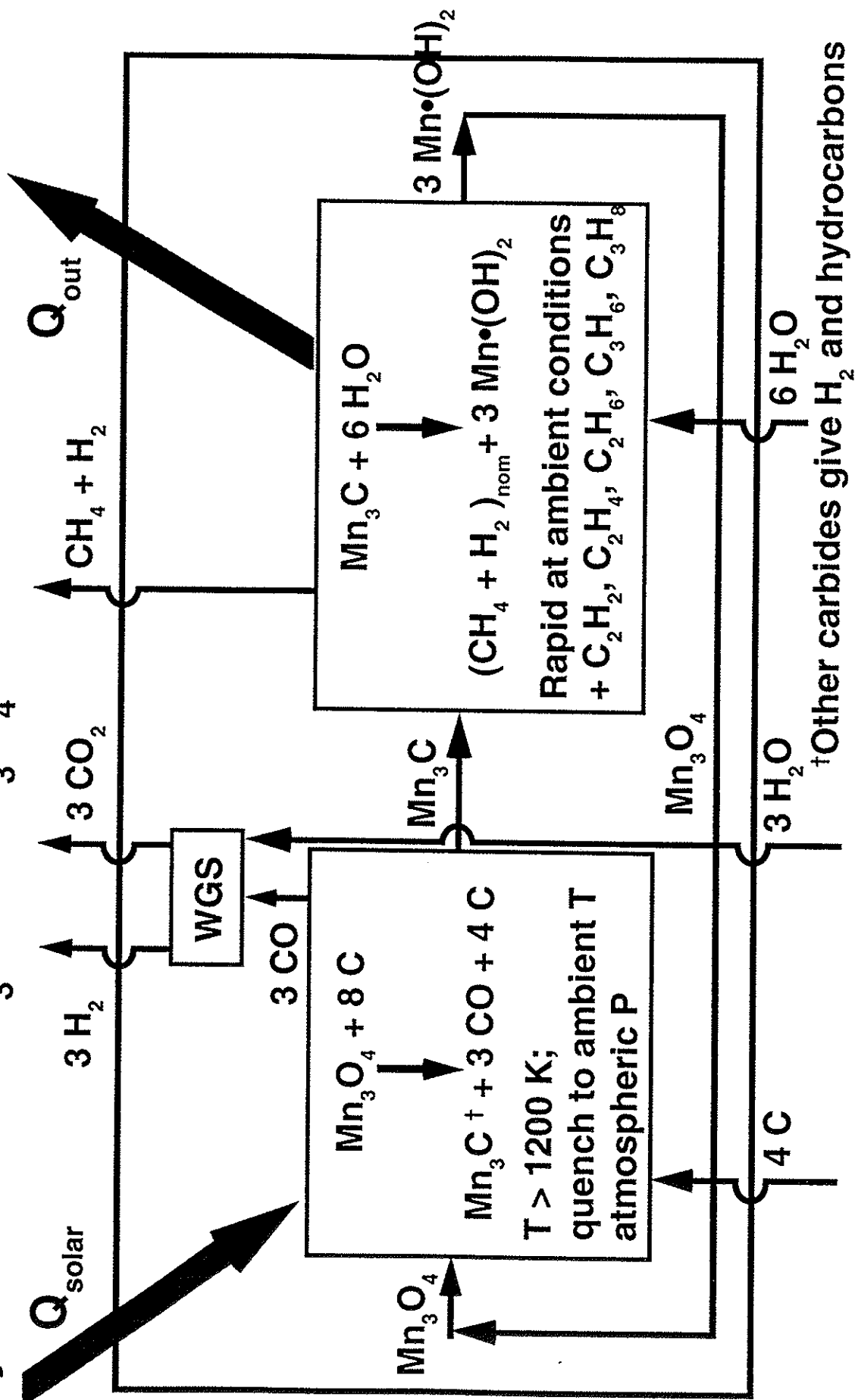




System #2: $\Delta G - \Delta H$

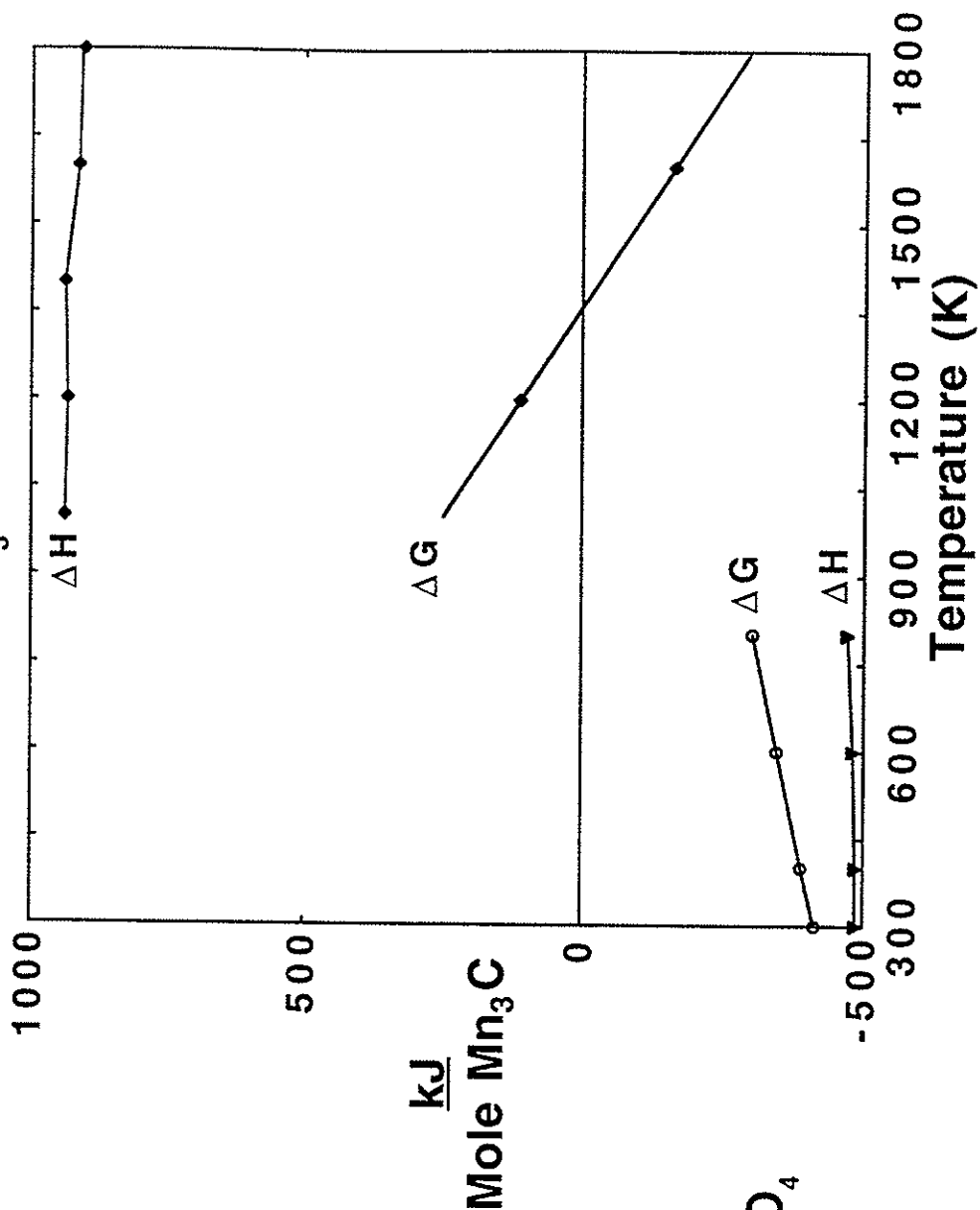
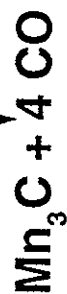
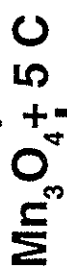


System #3: $\text{Mn}_3\text{C} - \text{Mn}_3\text{O}_4$

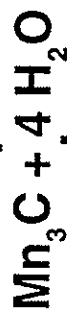


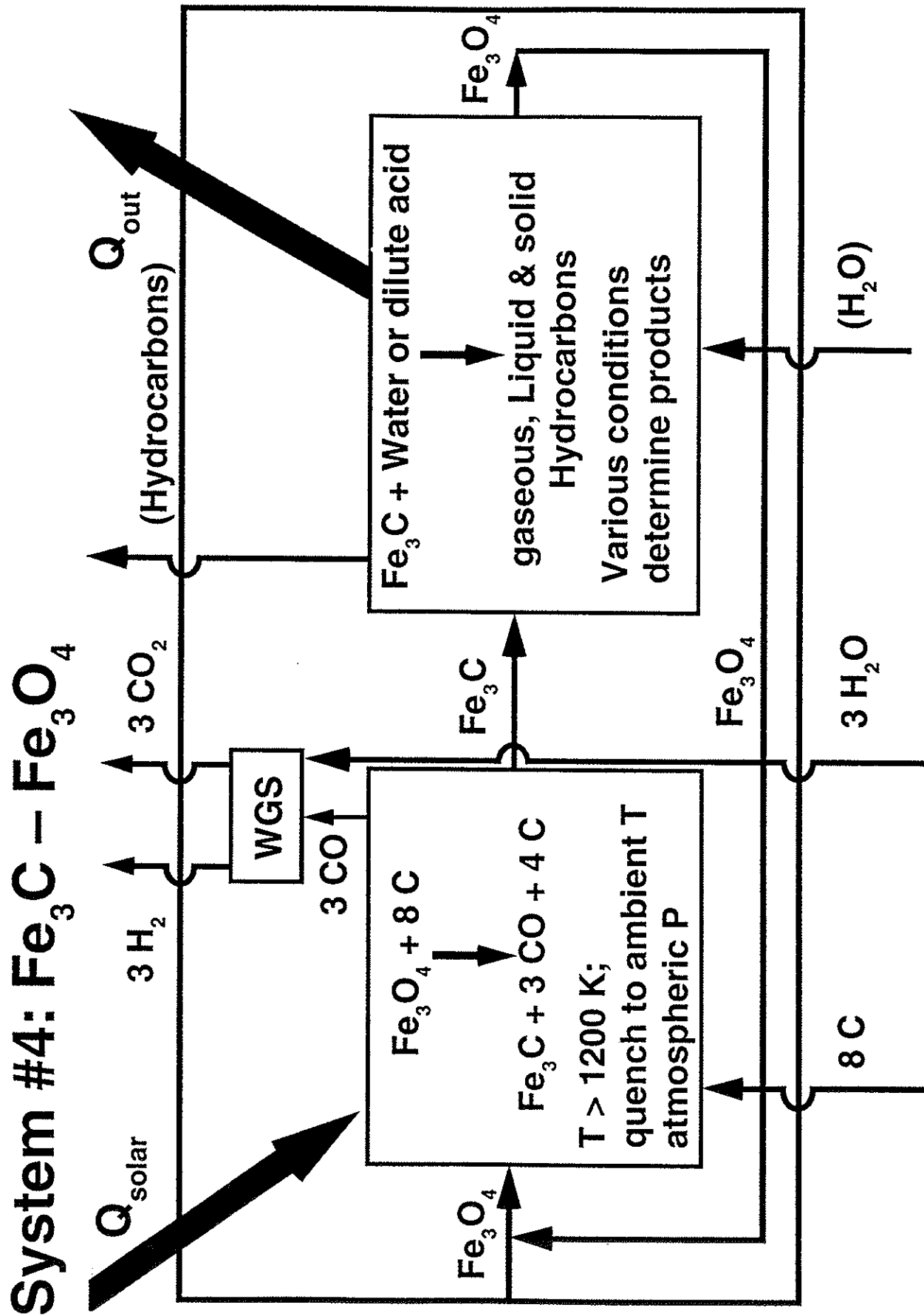
System #3: $\Delta G - \Delta H$

High-Temperature



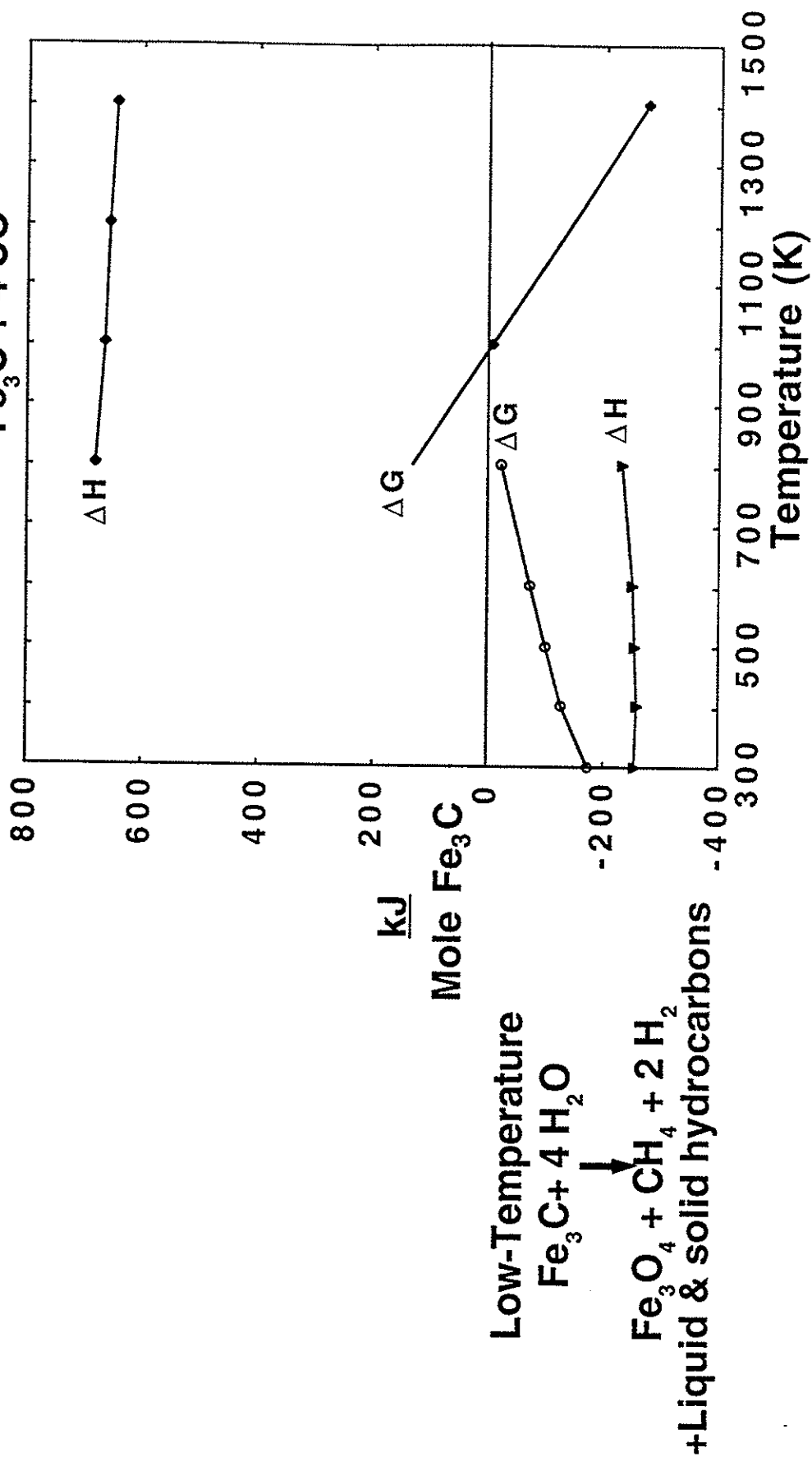
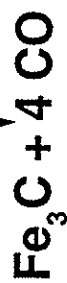
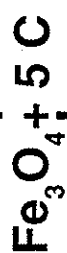
Low-Temperature





System #4: $\Delta G - \Delta H$

High-Temperature

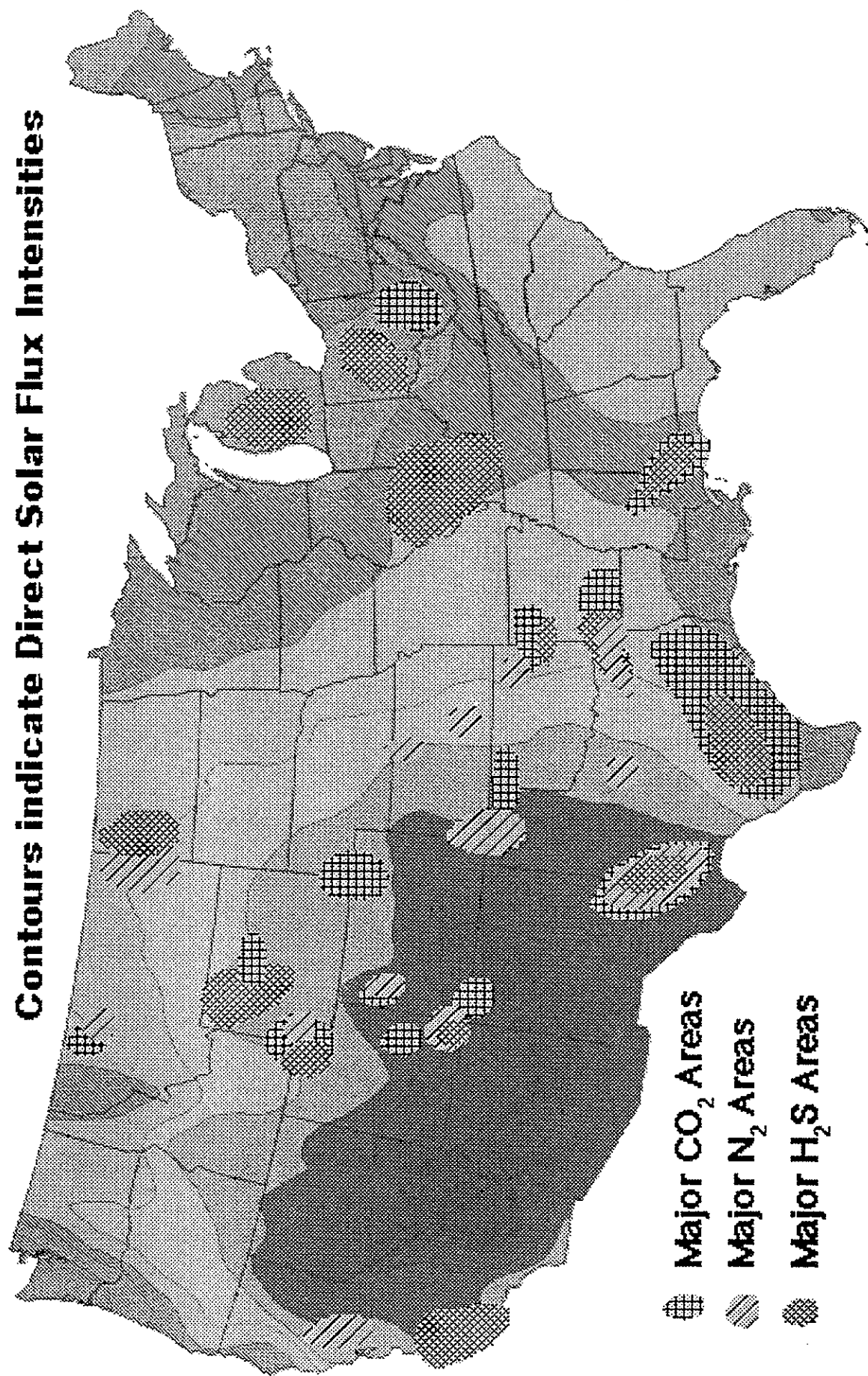


Other Routes to Carbides:

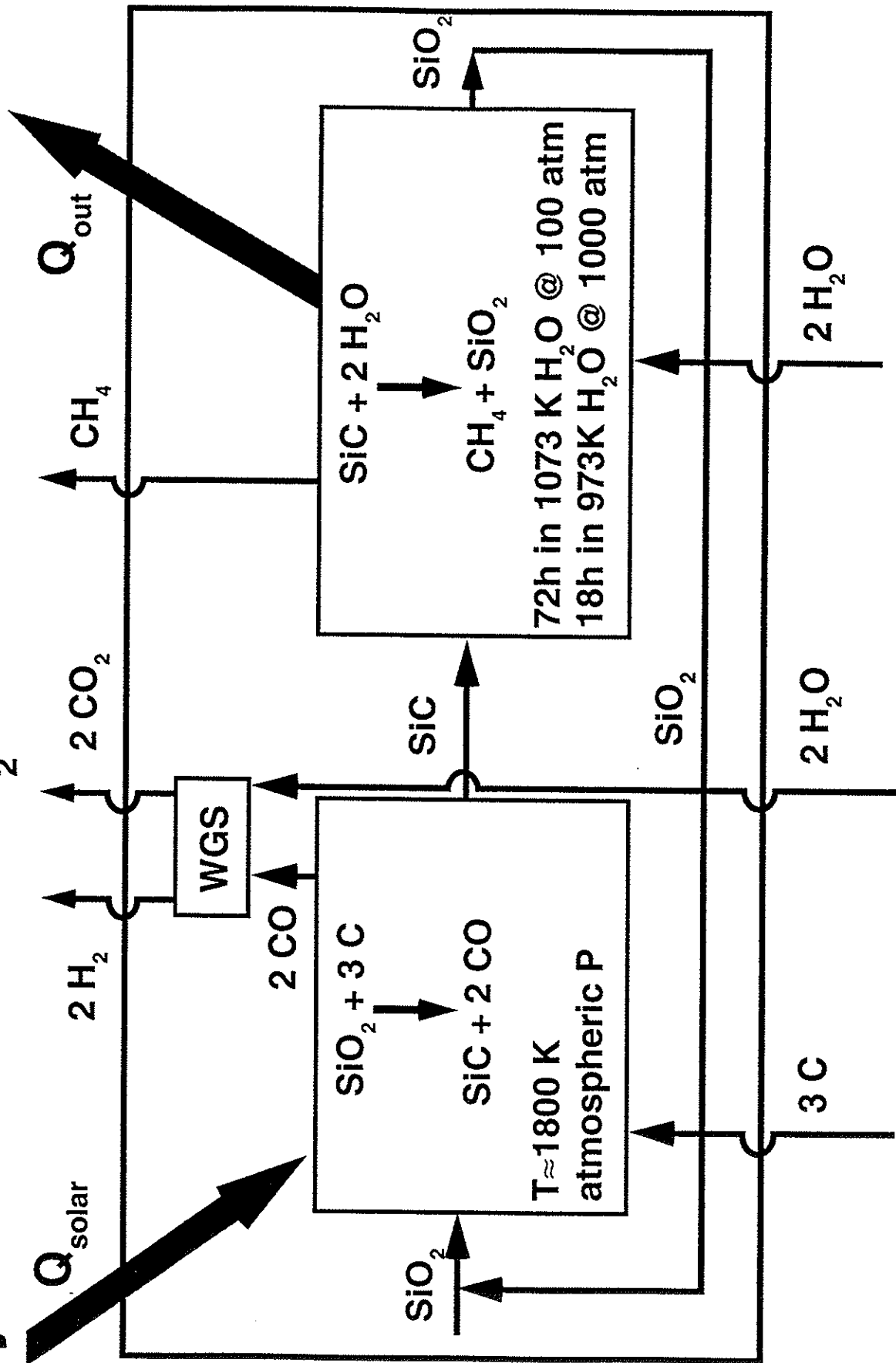
react oxides with methane-carbon dioxide

Subquality Natural Gas Deposits for U.S.

Contours indicate Direct Solar Flux Intensities

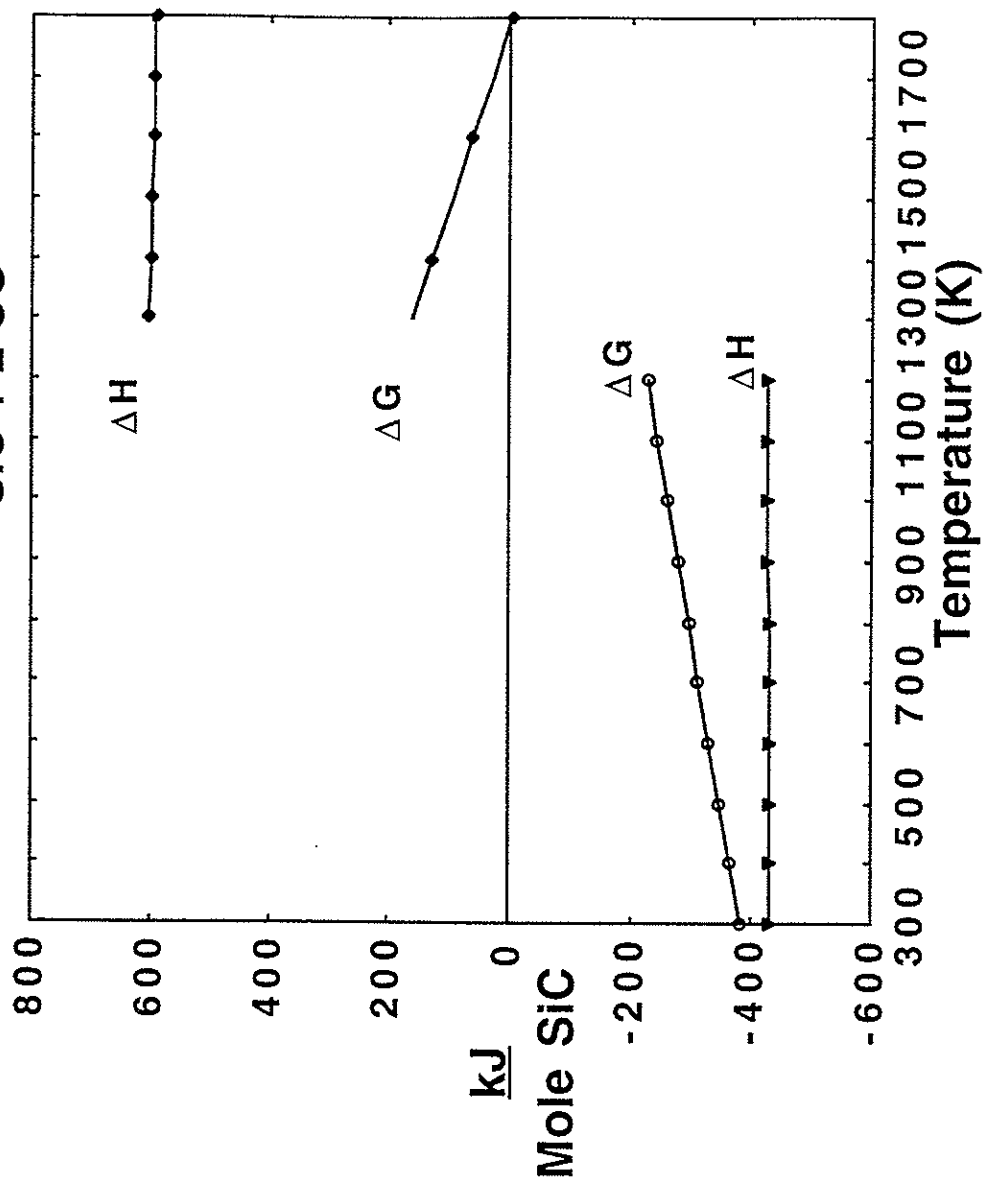
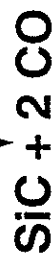
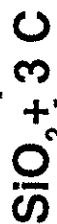


System #5: SiC – SiO₂

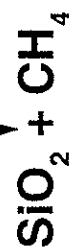
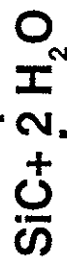


System #5: $\Delta G - \Delta H$

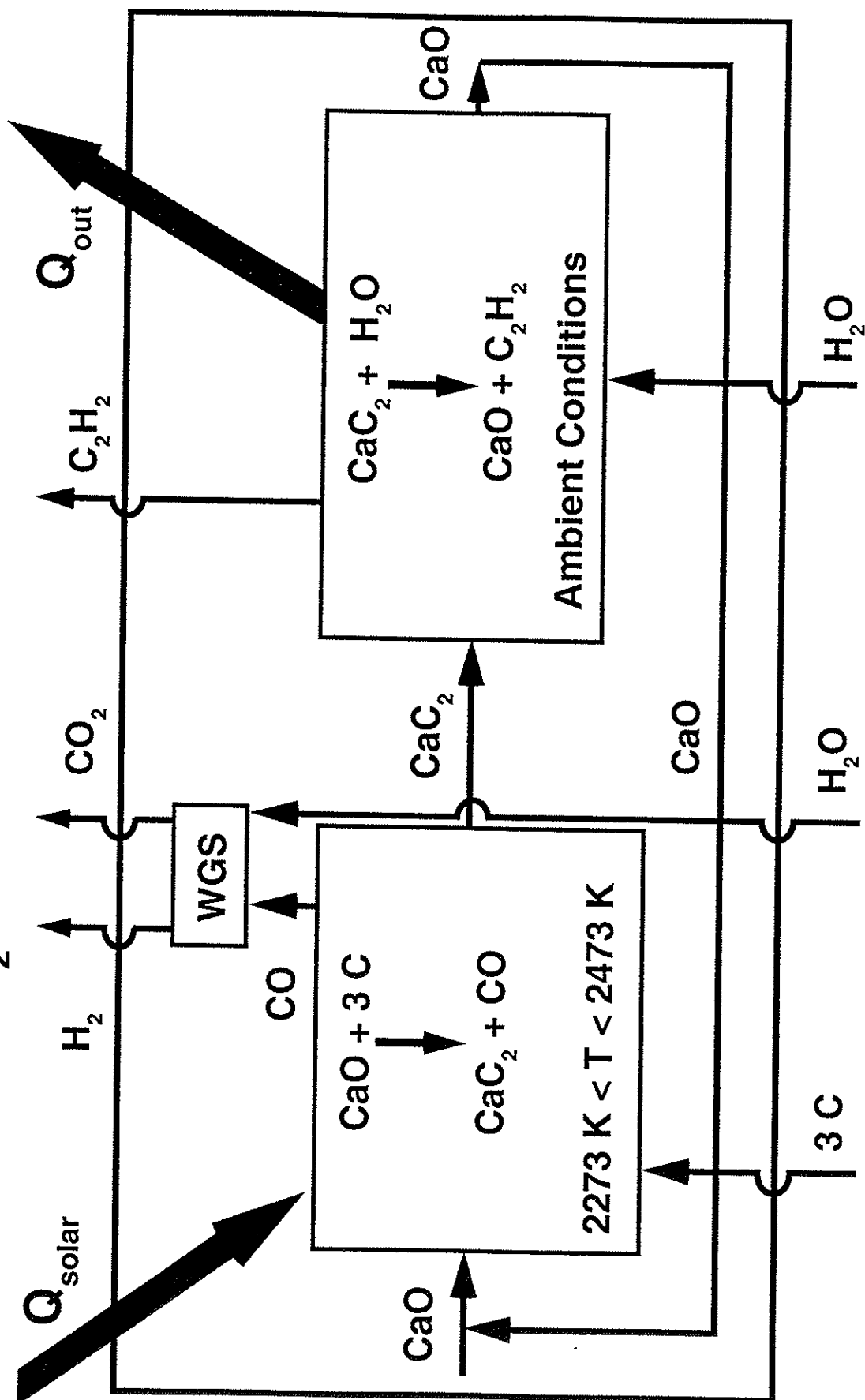
High-Temperature



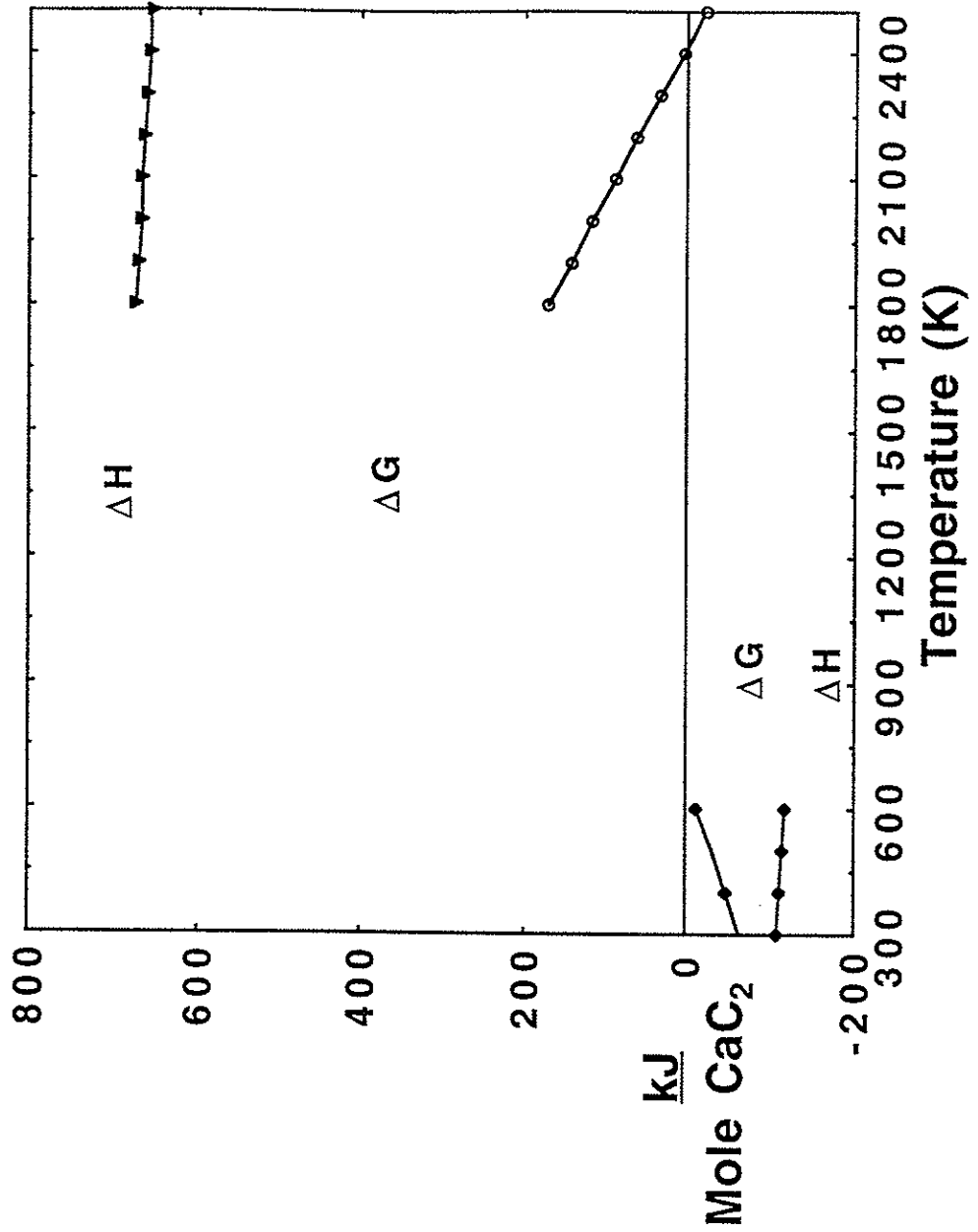
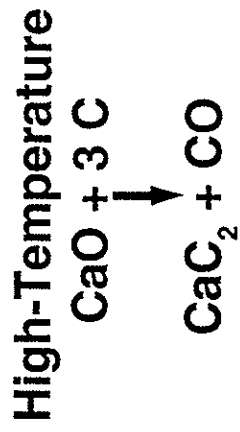
Low-Temperature



System #6: $\text{CaC}_2 - \text{CaO}$



System #6: $\Delta G - \Delta H$



Conclusions: systems of immediate interest

- Mn_3O_4 - Mn_3C
- Fe_3C cycle-combine with Fe_2O_3 water-splitting cycle
 - Require practical solar process temperatures
 - gas-solid reactions
 - can be joined with other H_2 -producing cycles
 - valuable hydrocarbon products
- **AIN- NH_3 cycle**
 - use alone or decompose the NH_3 for H_2 production

Approaches to High-Temperature Solar Destruction of Hazardous Wastes

Karl-Heinz Funken

German Aerospace Research Establishment (DLR)

Energy Technology Division

D-51140 Köln

Germany

Research and development in Solar Chemistry intends to establish useful applications of concentrated solar radiation for industrial chemical processes. The long term goal is the chemical storage of solar energy. For the short to mid term future some market niches can already be identified today. Examples of solar detoxification of hazardous wastes are discussed.

1. Direct absorption of concentrated solar radiation for the recovery of waste sulfuric acid.

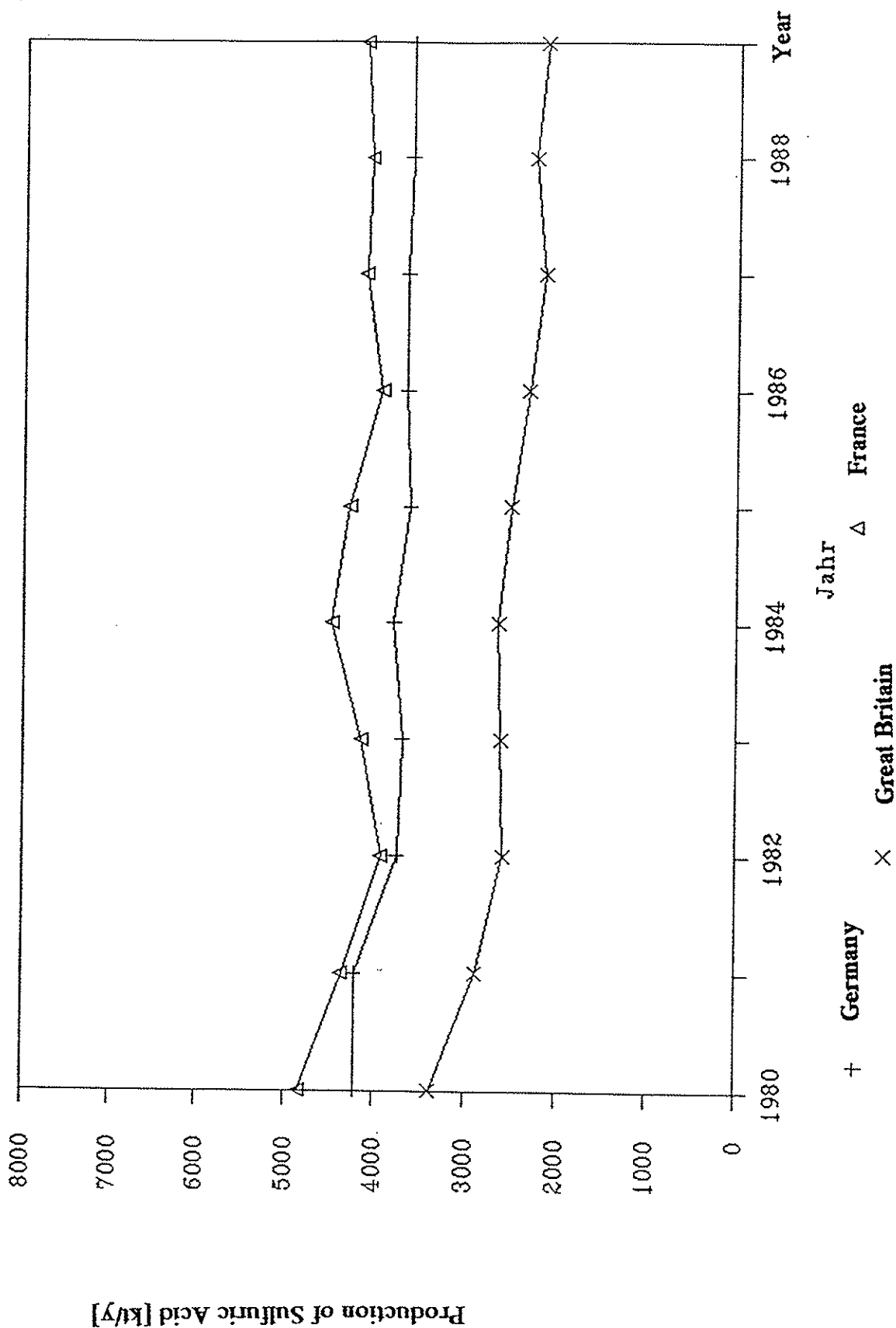
Sulfuric acid is one of the most important basic chemicals being used in numerous chemical and metallurgical processes. In many cases the acid ends up as a waste by-product highly loaded with organic impurities. Often dumping of the waste acid cannot be accepted due to environmental reasons, thus it has to be recycled. In the conventional fossil fired reprocessing plants the impurities are oxidized at high temperatures or by the addition of an oxidizer. The recovery techniques require a high specific energy input being appr. 6.36 MJ per kg sulfuric acid (70 %) or appr. 2.5 MWh per ton. We investigated how concentrated solar radiation could beneficially be used for the recovery of waste sulfuric acid. In a direct absorbing aerosol receiver-reactor the waste acid is irradiated with concentrated radiation applying oxidizing conditions. The results show a higher oxidation rate as compared to pure thermal heating. In solar plants employed for the recovery of waste sulfuric acid the use of a direct absorption receiver-reactor is advantageous because a higher oxidation rate can be achieved than in an indirectly heated receiver-reactor.

2. Radiatively heated rotary kiln for the high temperature treatment and detoxification of wastes.

In the flue gas cleaning units of waste incineration plants filter dusts remain as a toxic residue; e.g. in Germany appr. 350.000 t/y and in Switzerland appr. 40.000 t/y. The vitrification of the dusts is an alternative for dumping. However, it is a highly energy consuming process requiring appr. 1-2 MWh electric current per ton material. Thus we investigated whether there is a chance to substitute the energy supply to a vitrification plant by solar radiation and a conceptual design of a pilot solar central receiver plant was created. A heliostat field focuses the solar radiation onto the aperture area of an open direct absorbing rotary kiln receiver-reactor which is placed on a tower in front of the heliostat field. The concentrated radiation illuminates the upper wall of the melting drum directly. A thin film of melted filter dust adhering to the wall receives the energy and transportes it to the bulk melt by rotation of the drum. At the high temperatures organic compounds are destroyed and volatile heavy metal compounds evaporize. To prevent the escape of dust and evaporized heavy metal salts through the open receiver-reactor to the environment a radiation duct is placed in front of the drum. An air stream is sucked through the radiation duct and the receiver-reactor. It is transporting the evaporized compounds to an off gas purification unit. The maximum amount of filter dusts which could be treated in the suggested pilot plant is about 300 kg/h and 550 t/y, respectively.

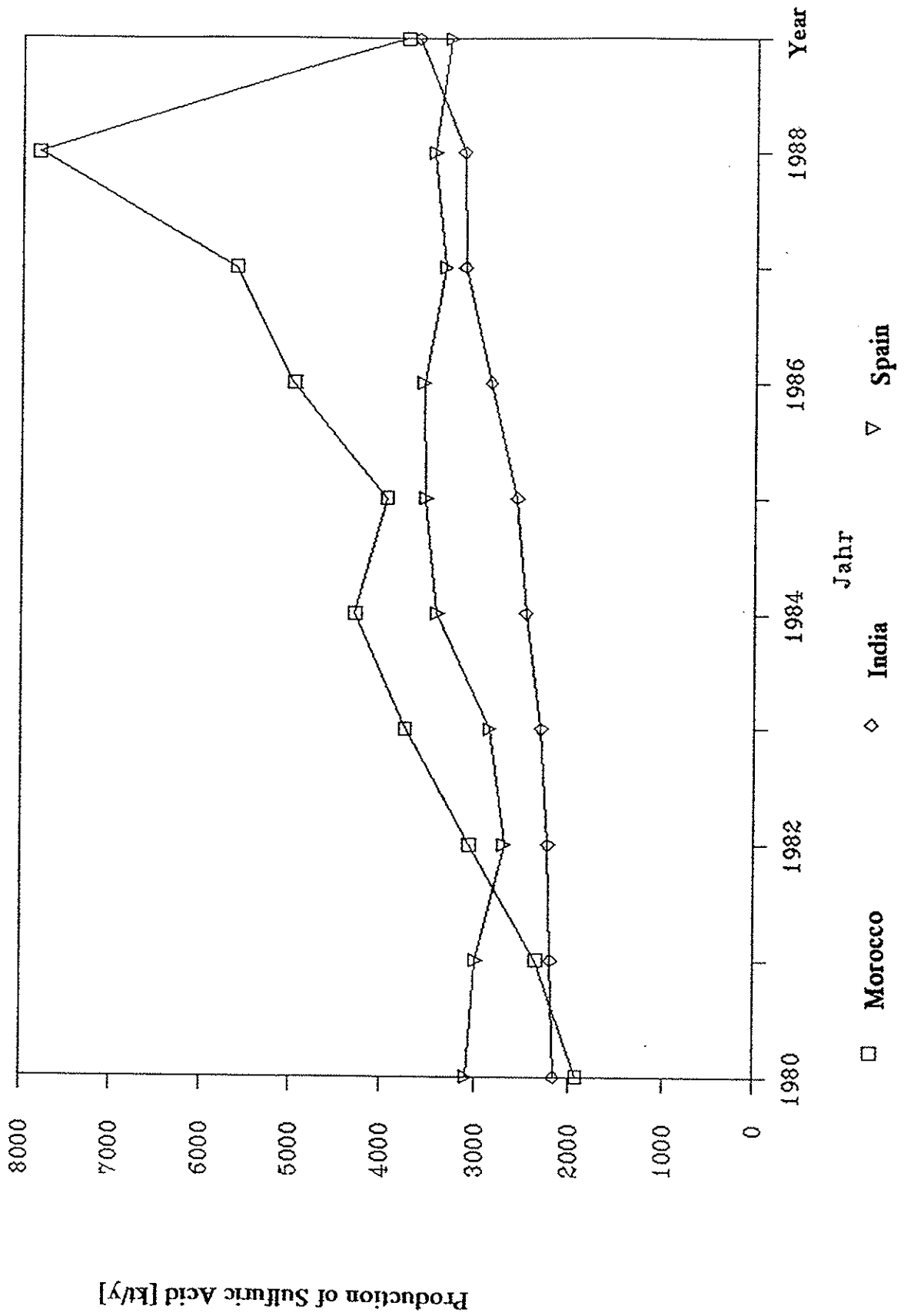


Production of Sulfuric Acid in Selected Industrialized Countries





Production of Sulfuric Acid in Selected Solar Countries

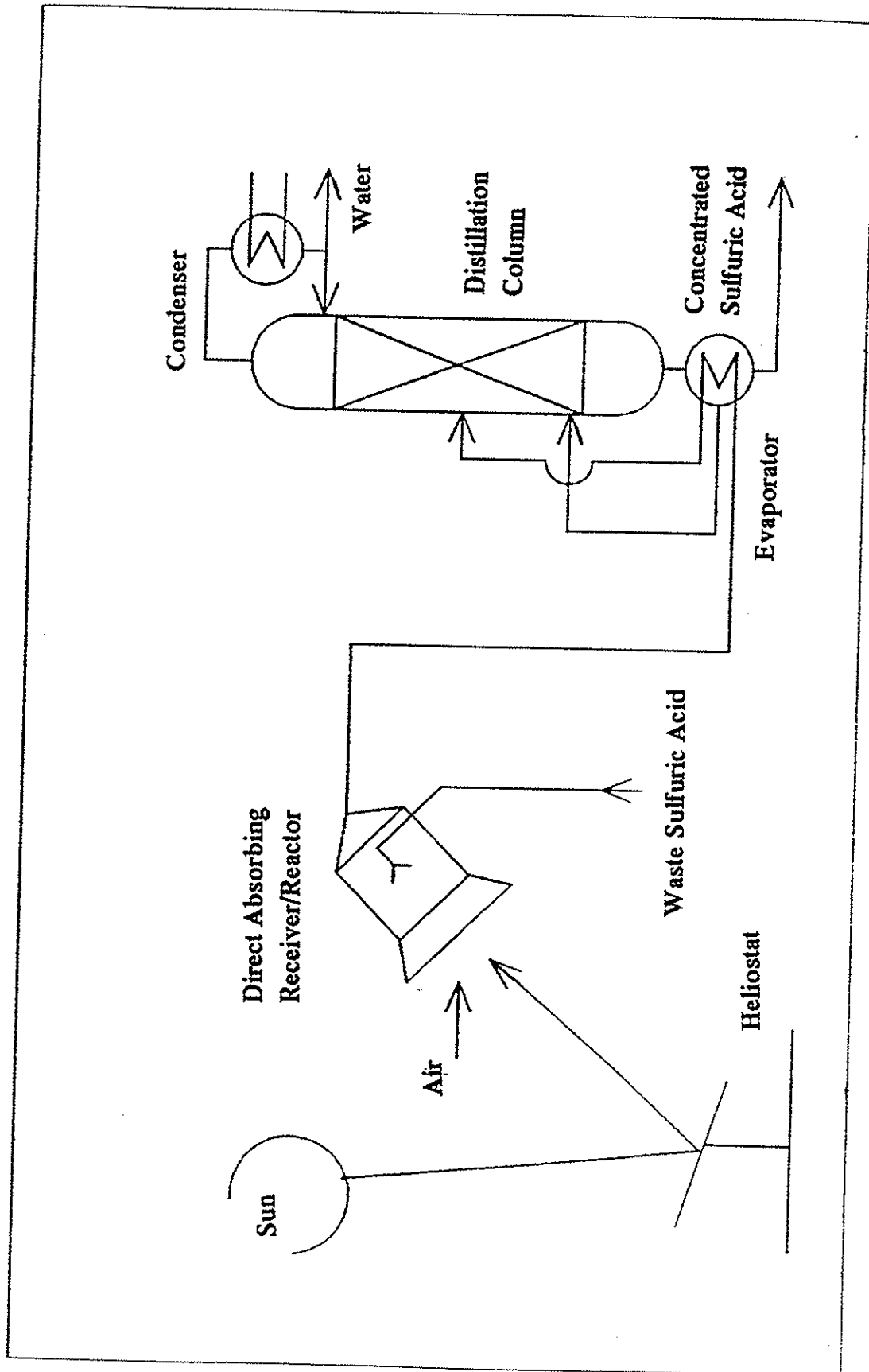


Theoretical Steps	Heat Demand [10 ⁹ J/t MH WSA]	Heat Demand [%]
1. Dehydration of 70 % H ₂ SO ₄	0.460	7.2
2. Evaporation of H ₂ O	0.967	15.2
3. Evaporation of H ₂ SO ₄	0.572	9.0
4. Heating from 20 °C to 340 °C	0.942	14.8
5. Dissociation of H ₂ SO ₄ : H ₂ SO ₄ = SO ₃ + H ₂ O	0.973	15.3
6. Dissociation of SO ₃ : SO ₃ = SO ₂ + 0.5 O ₂	0.991	15.6
7. Heating from 340 °C to 1000 °C	1.455	22.9
Total	6.360	100

Specific Heat Demand for the Thermal Dissociation of Sulfuric Acid at 1000 °C

Feed Concentration 70 wt% H₂SO₄.

t MH WSA: tons Mono Hydrate and 100 % H₂SO₄ respectively as diluted Waste Sulfuric Acid acc. to Sander (1978)



General Scheme for a Solar Waste Sulfuric Acid Recovery Plant

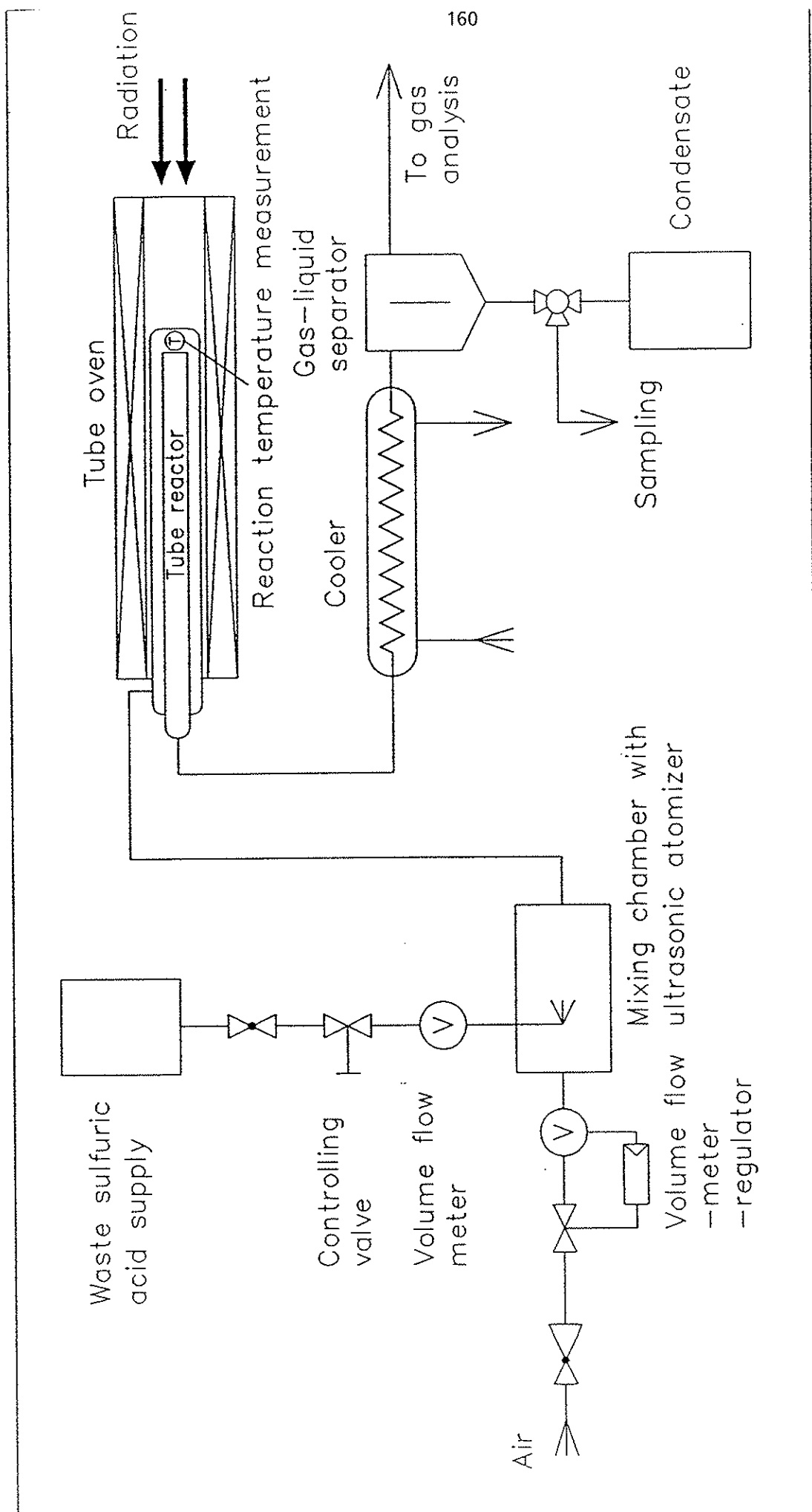


Figure 1 Schematic testing device

Deutsche Forschungsanstalt für Luft- und Raumfahrt e.V.

Schematic types of waste acid receiver-reactors



Fig.1: direct absorption receiver-reactor

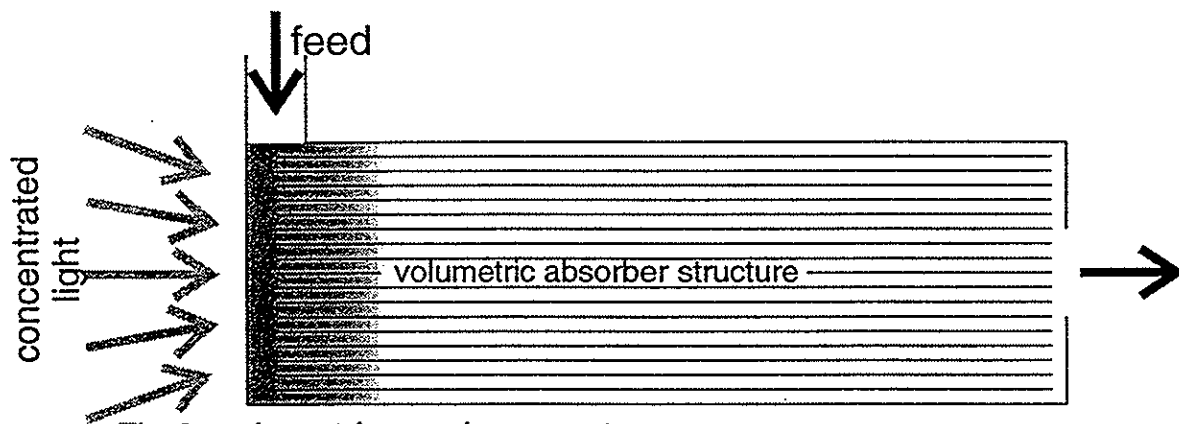


Fig.2: volumetric receiver-reactor

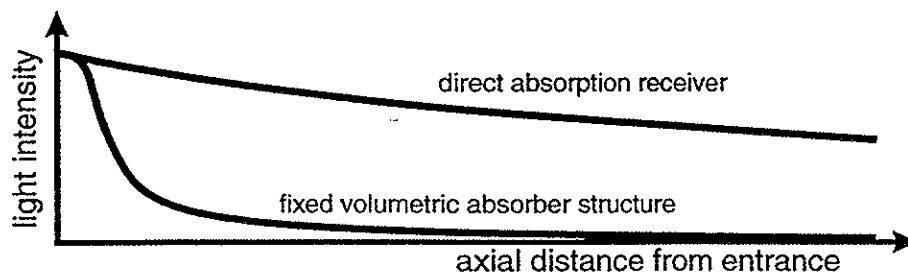
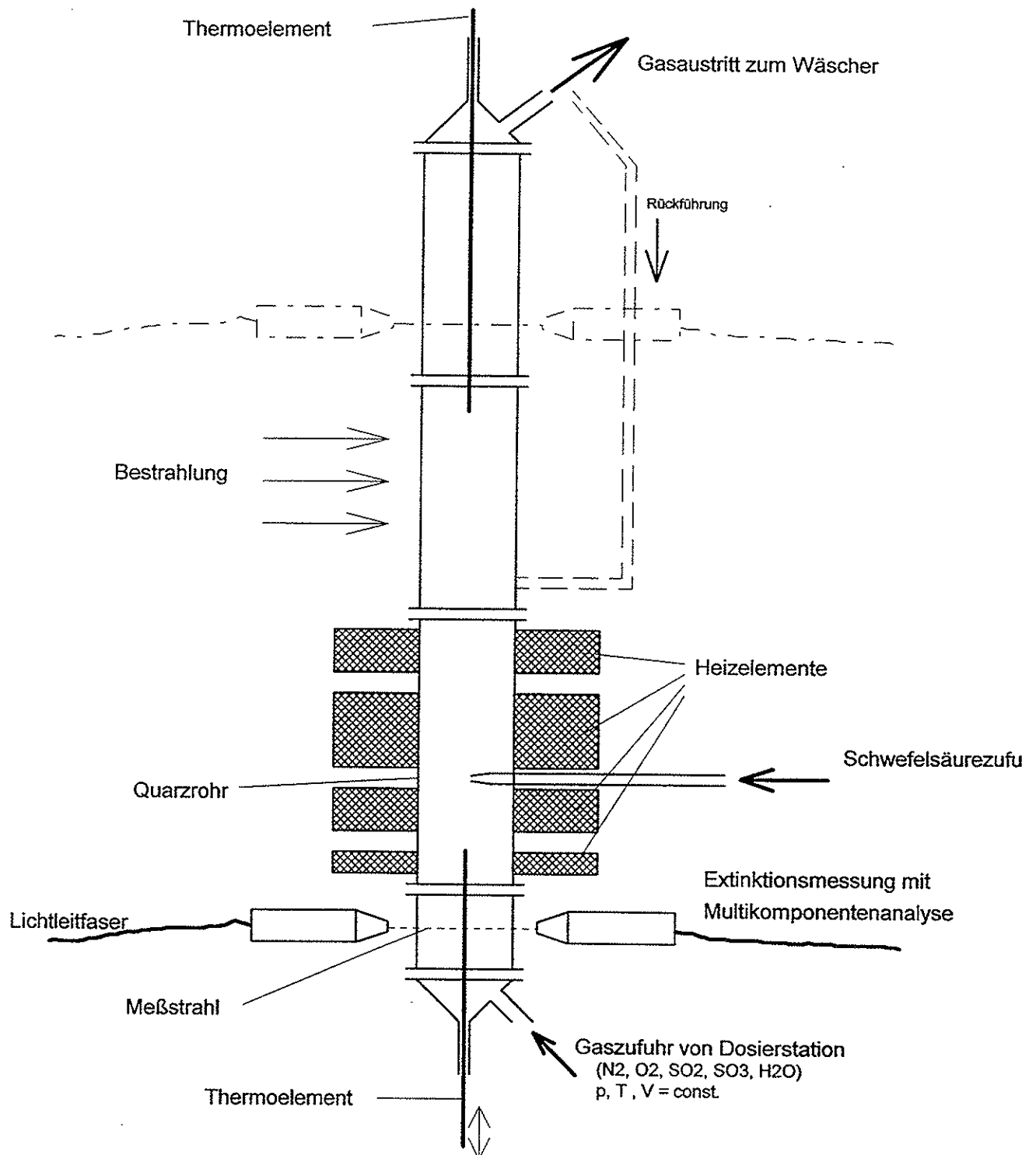


Fig.3: light intensity decrease as a function of axial distance



Skizze des Versuchsreaktors zur Schwefelsäurespaltung

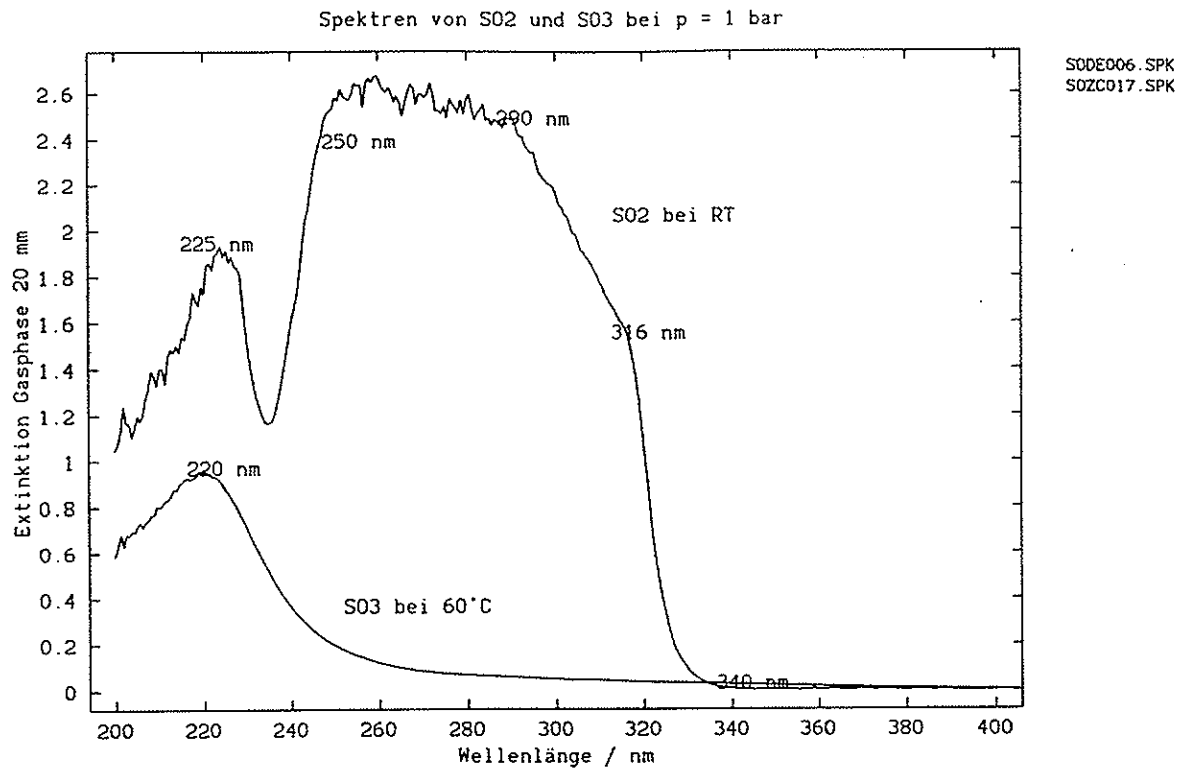


Bild 2: Spektren von SO₂ und SO₃, gemessen im Versuchsreaktor bei Umgebungsdruck.

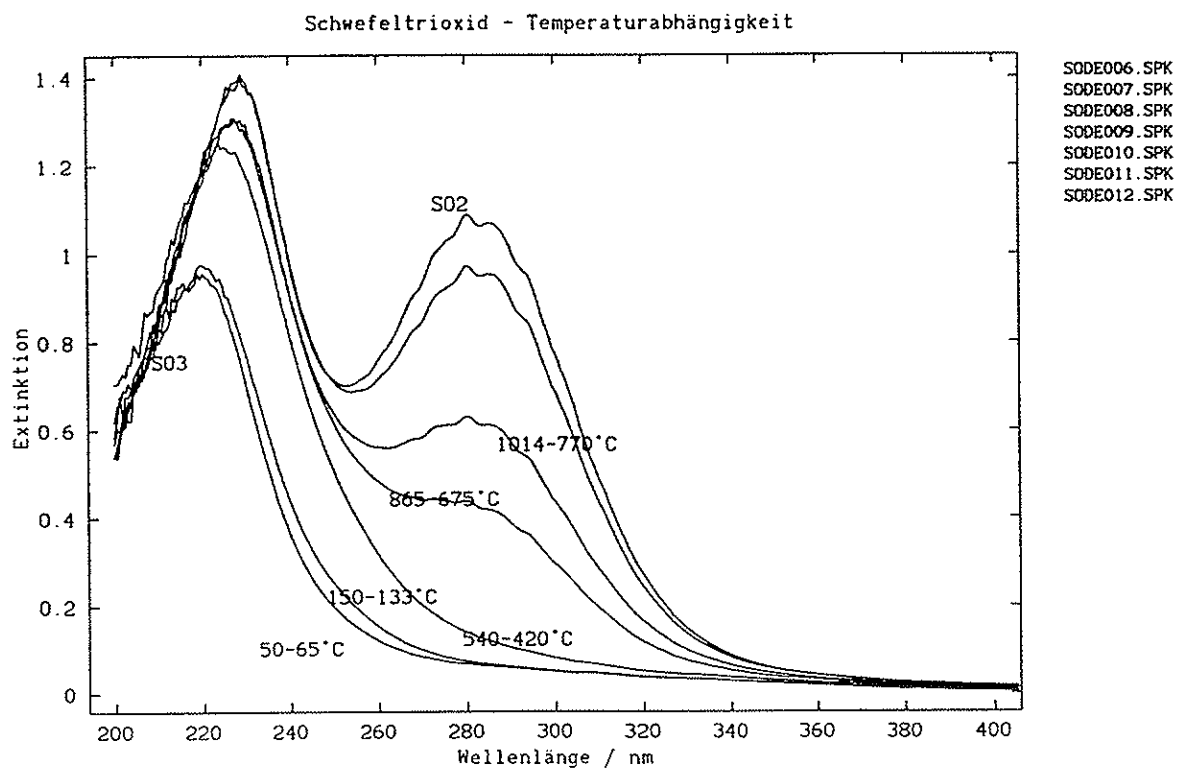
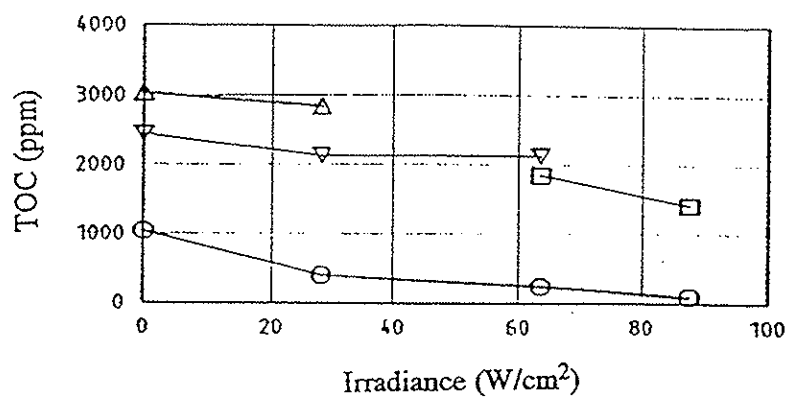
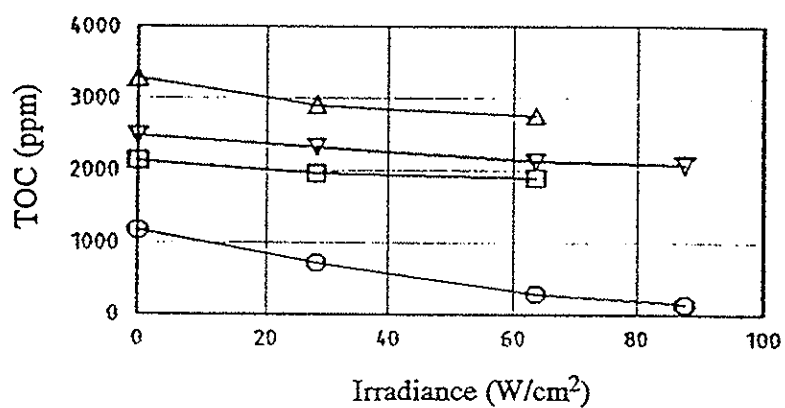


Bild 3: Temperaturabhängigkeit des SO₃-Spektrums bei Umgebungsdruck

(a)

 $m_{wa}=0.2 \text{ l/h}$

(b)

 $m_{wa}=0.3 \text{ l/h}$

(c)

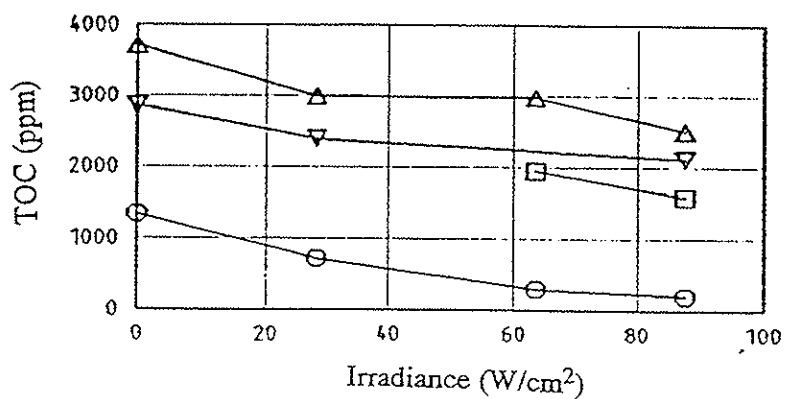


Figure 4 TOC-concentration of the condensate vs. the irradiance for different volume flows of liquid waste sulfuric acid and reaction temperatures:
 Δ : $\vartheta=500^\circ\text{C}$, ∇ : $\vartheta=600^\circ\text{C}$, \square : $\vartheta=700^\circ\text{C}$, \circ : $\vartheta=800^\circ\text{C}$.

$$c_{\text{TOC}} = f_1[m_{\text{wa}}, \exp(a_1/T_{\text{eff}})]$$

m_{wa} : volume flow waste acid

T_{eff} : effective reaction temperature

$a_1 = E/R$ to describe an activation energy

$$a_1 = 11.3 \cdot 10^3 \text{ K}$$

$$E = 91.7 \text{ kJ/mol}$$

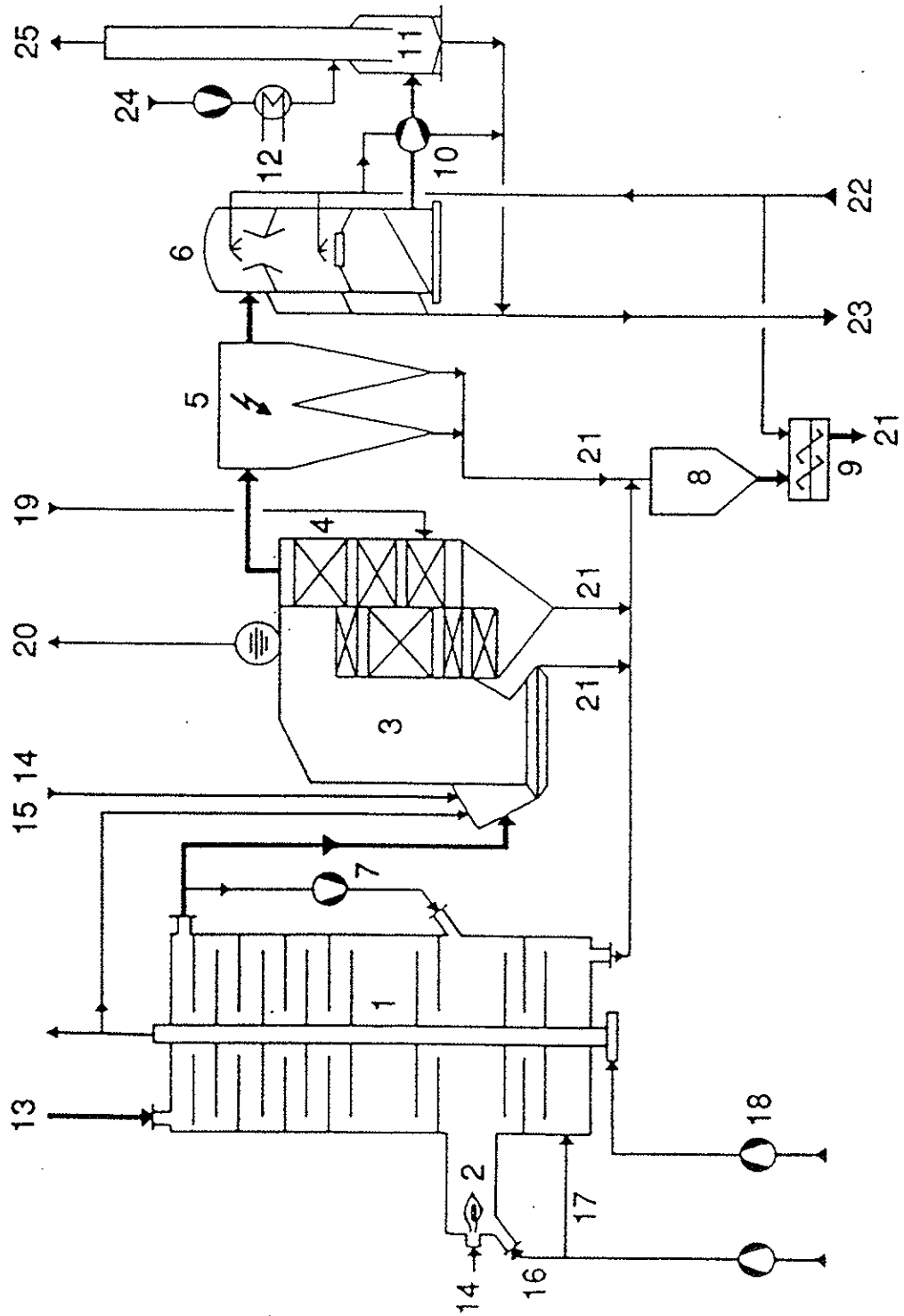
$$T_{\text{eff}} = T_{\text{R}} + \Delta T_{\text{I}}$$

$$\Delta T_{\text{I}} = f_2(I, T_{\text{R}}, m_{\text{ma}}); \Delta T_{\text{I}}(I=0) = 0$$

T_{R} : reaction temperature

ΔT_{I} : radiation-induced temperature increase

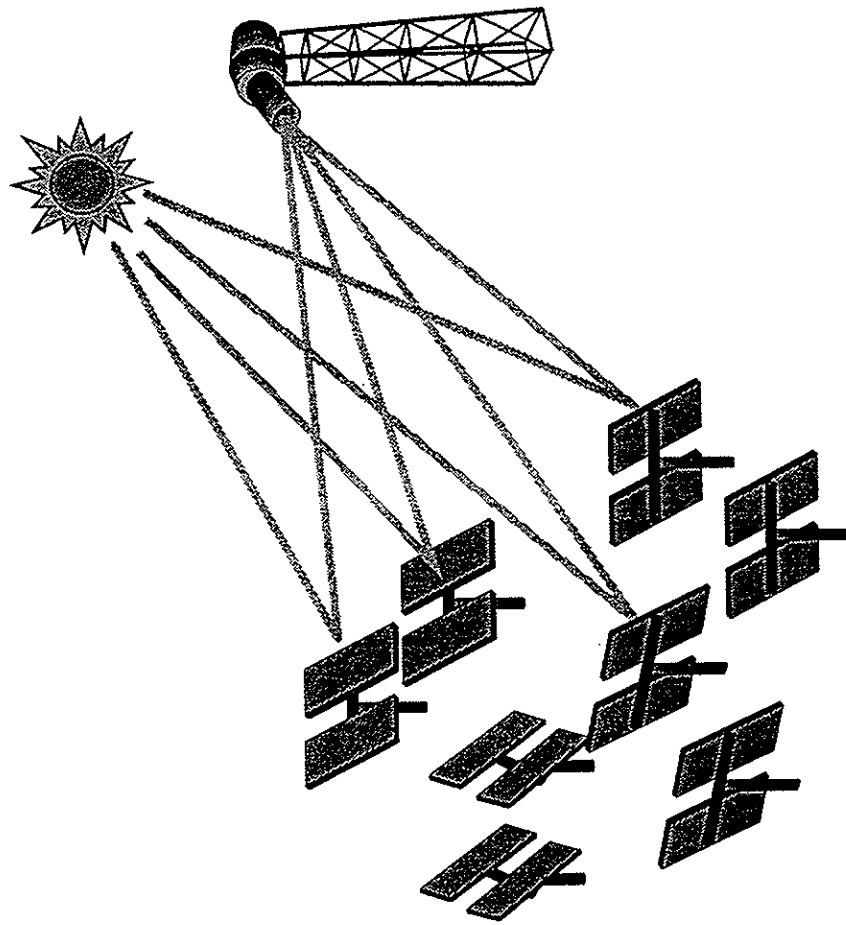
I : Irradiance



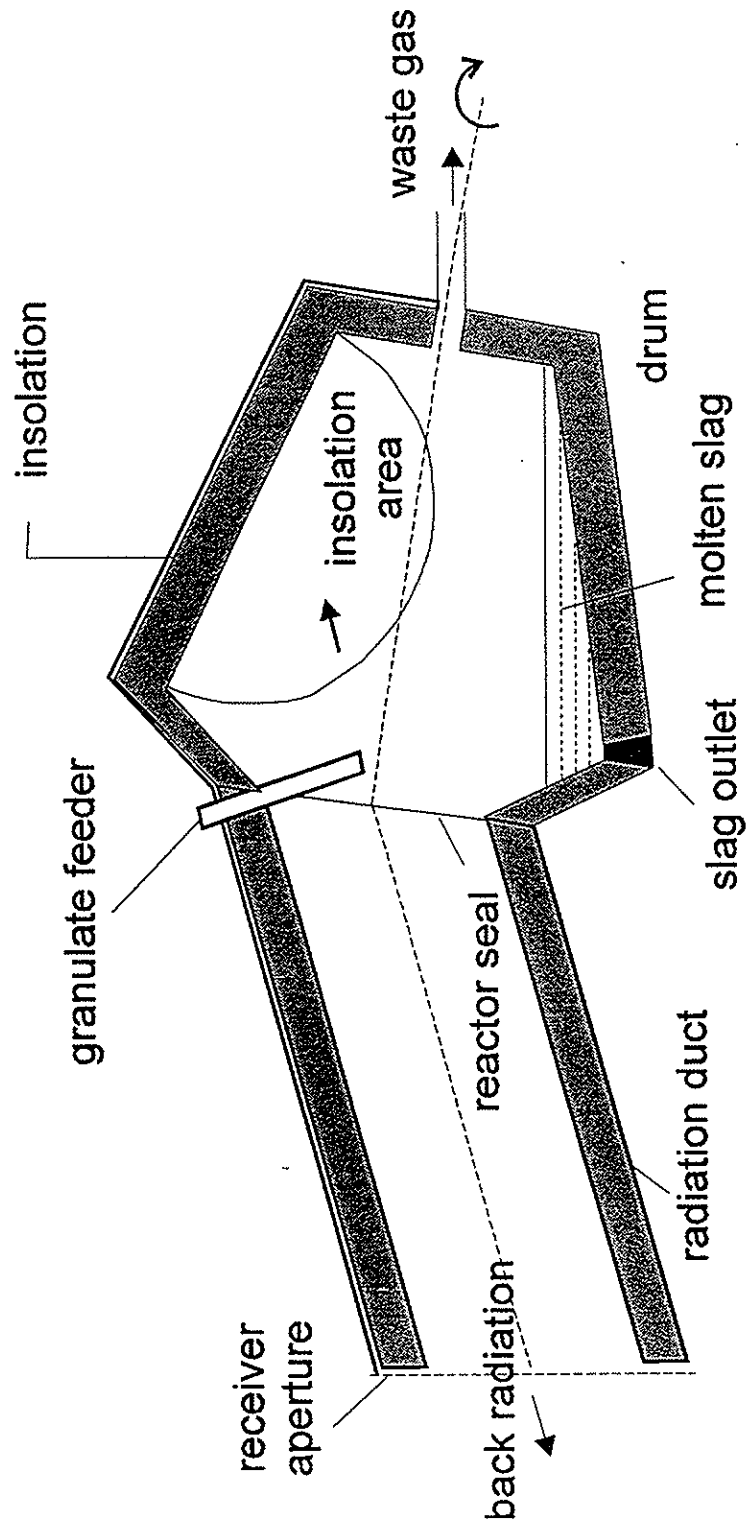
Deutsche Forschungsanstalt für Luft- und Raumfahrt e.V.

Expected Advantages of Solar High Temperature Destruction of Hazardous Wastes as Compared to "Conventional" Treatment

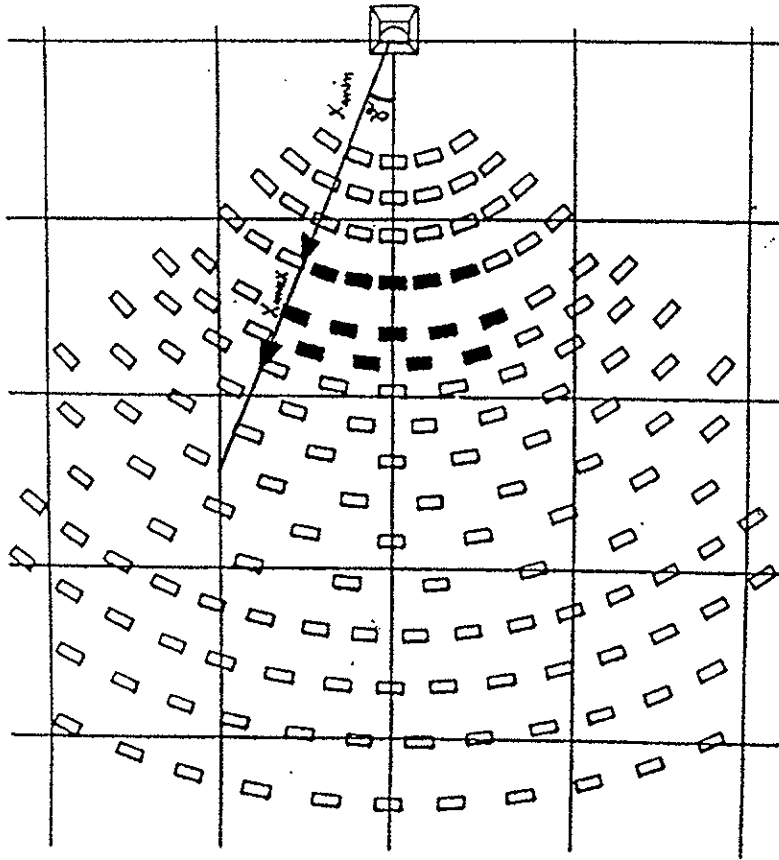
- no fossil fuel required**
- less excess air required**
- less gas volume to be heated**
- less gas volume to be treated after high temperature treatment**
- less emissions of off-gases**
- lower temperatures**
- higher concentrations of toxic materials**
- direct irradiation of toxic materials: higher heat flux densities**



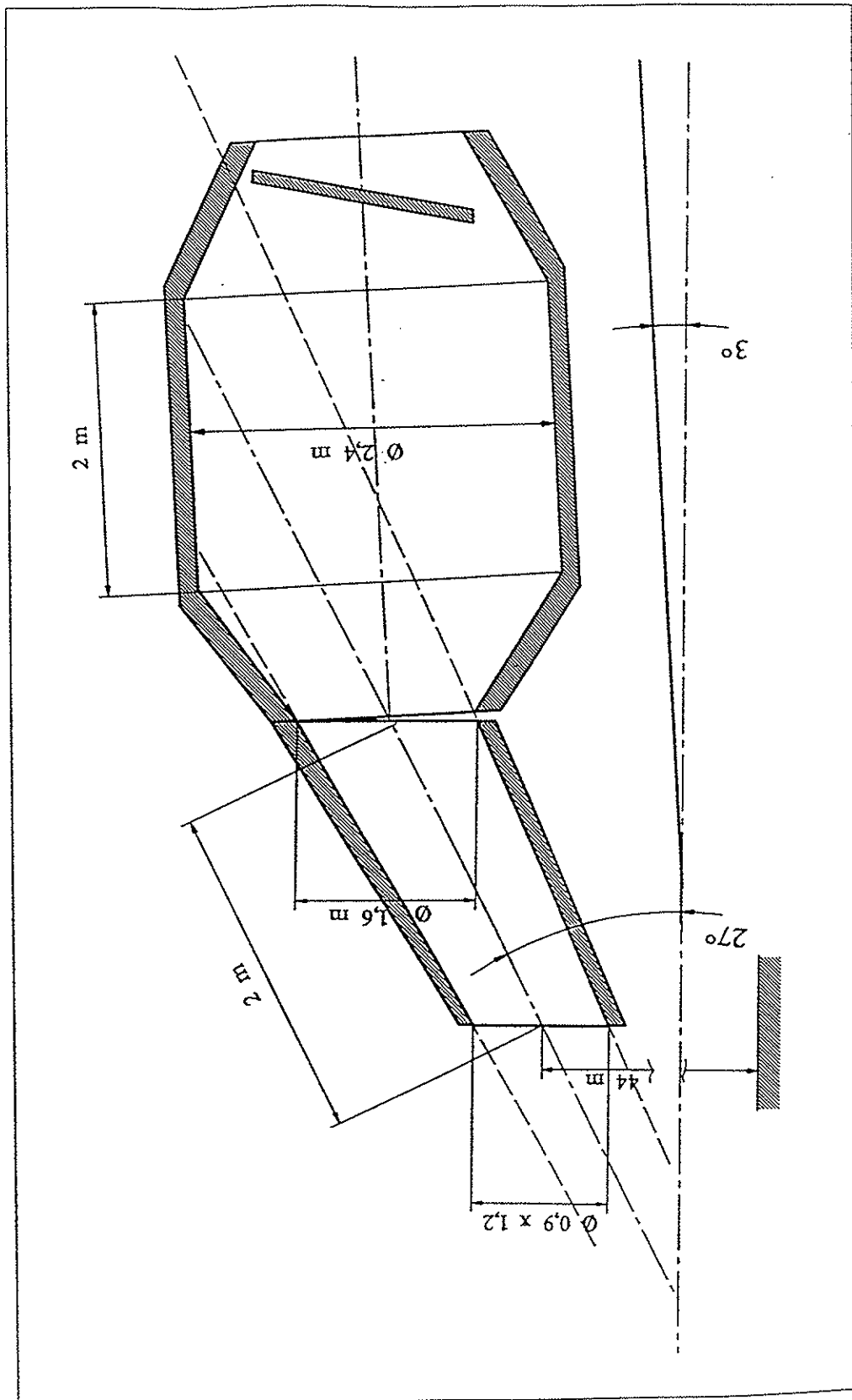
Plant scheme for the high temperature treatment of filter dusts

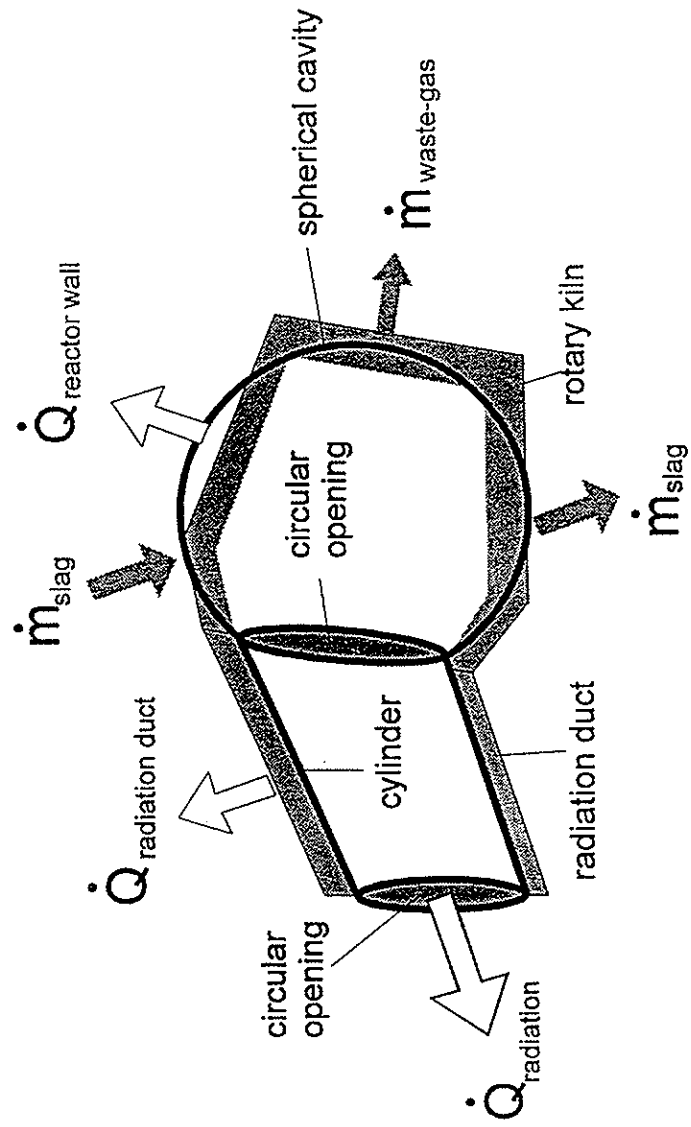


Rotary kiln receiver/reactor

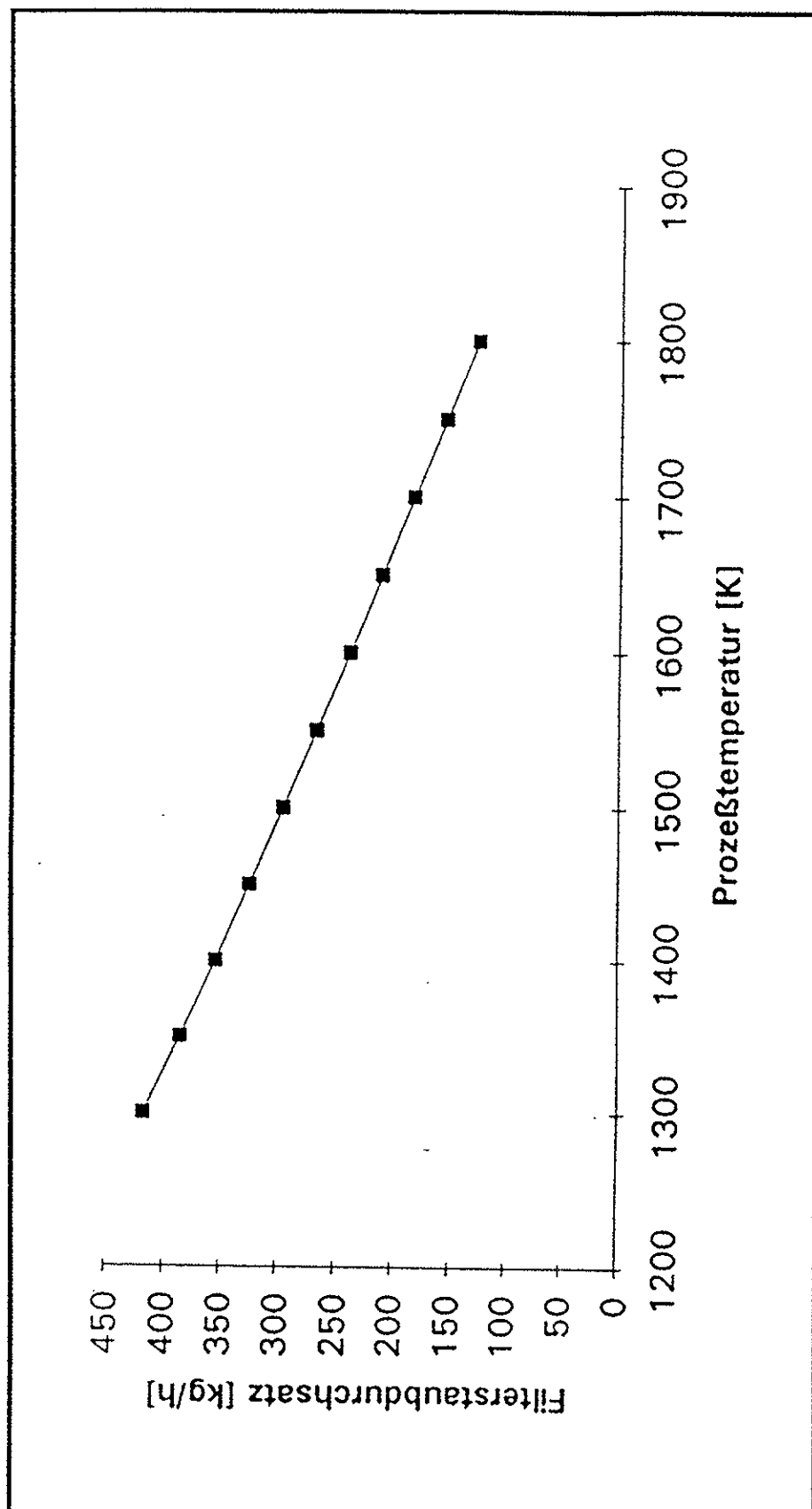


useable heliostats of the SSPS-field

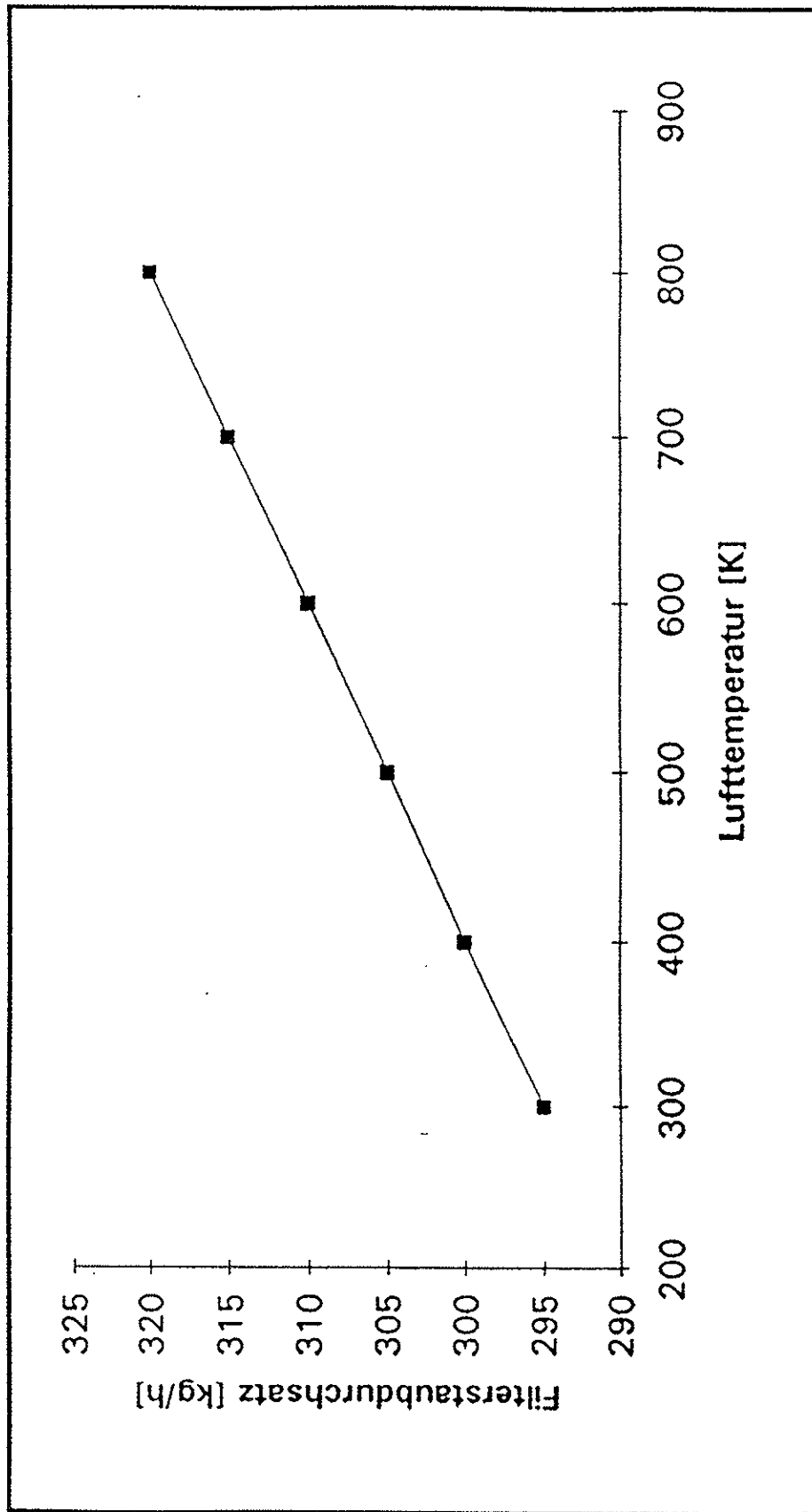




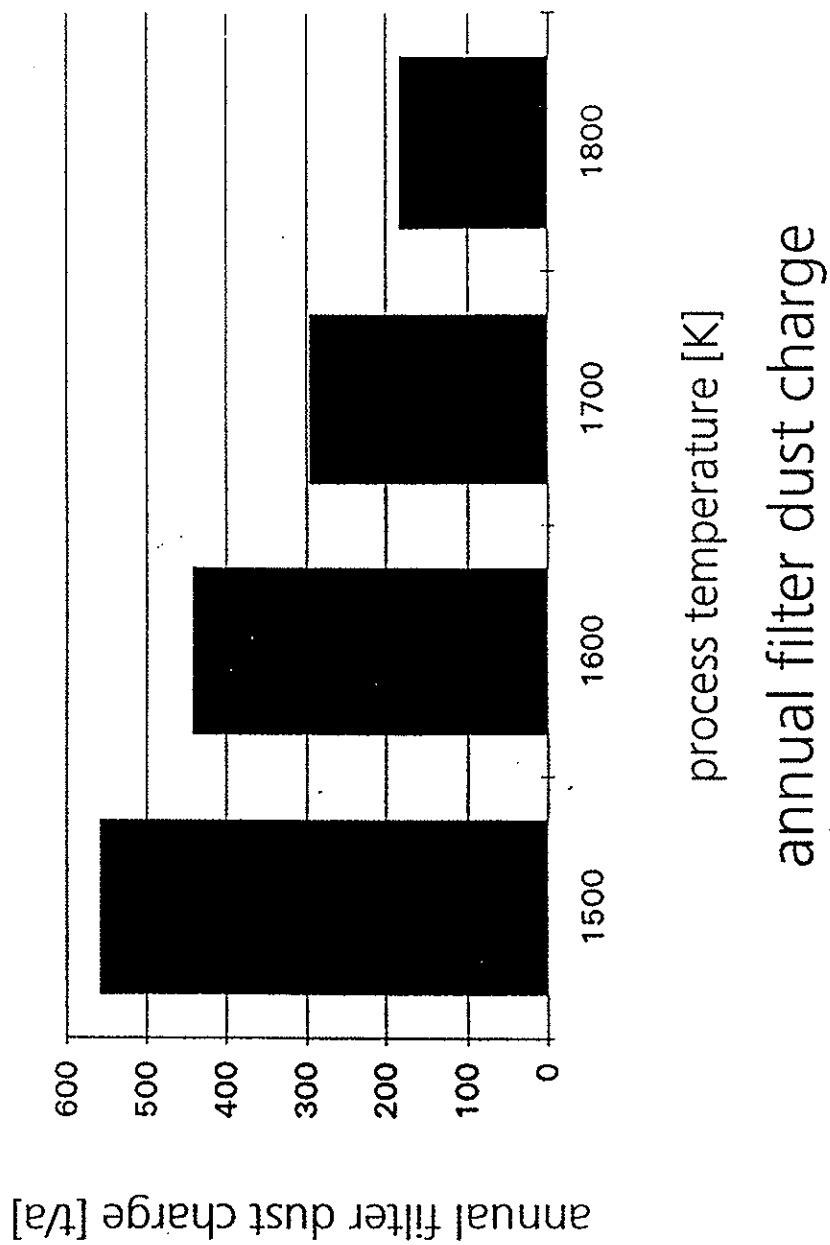
Model for the energy balance of the rotary kiln



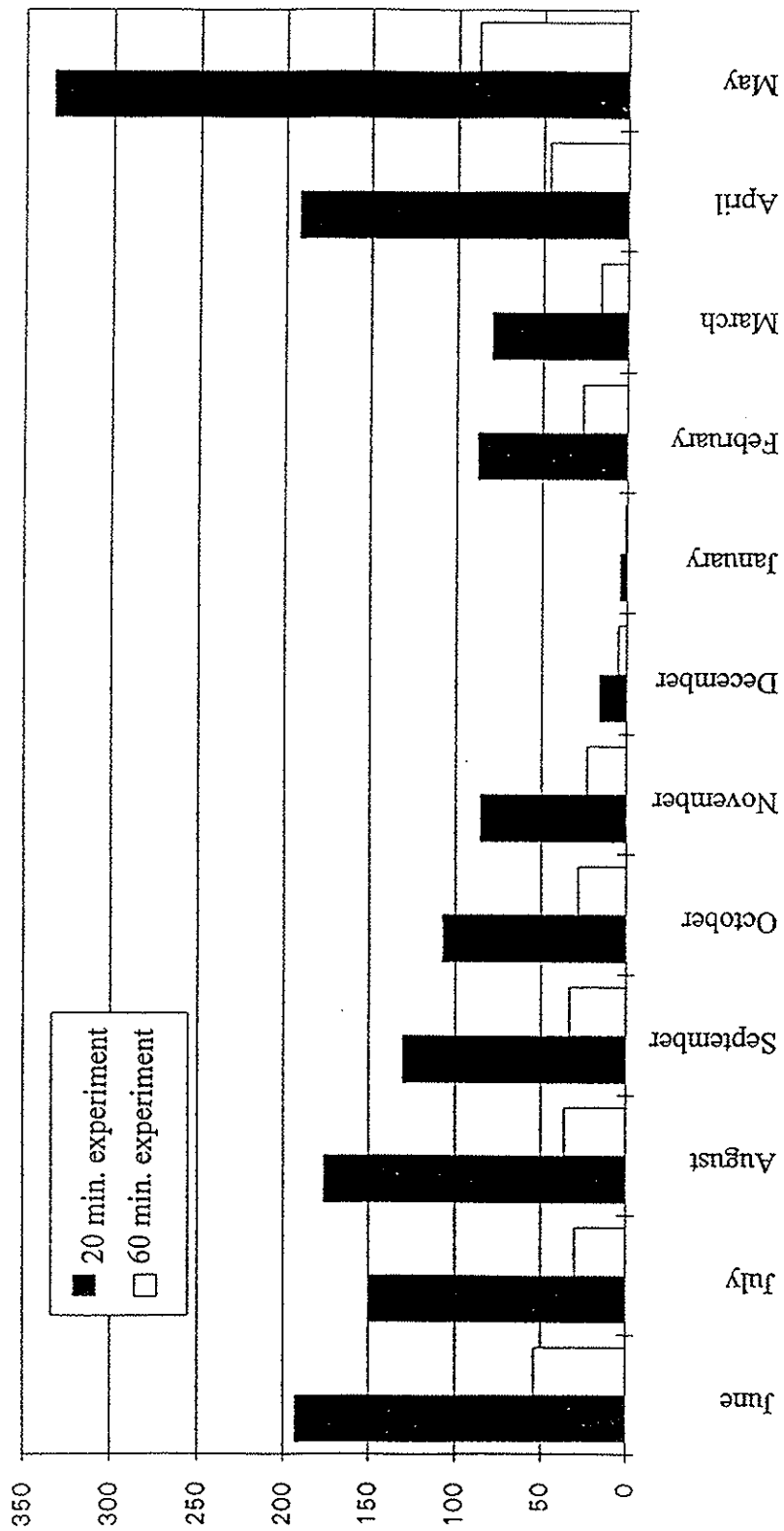
Abhängigkeit des Filterstaubdurchsatzes bei
verschiedenen Prozeßtemperaturen



Abhängigkeit des Filterstaubdurchsatzes von
der Luftvorwärmung



Number of experiments



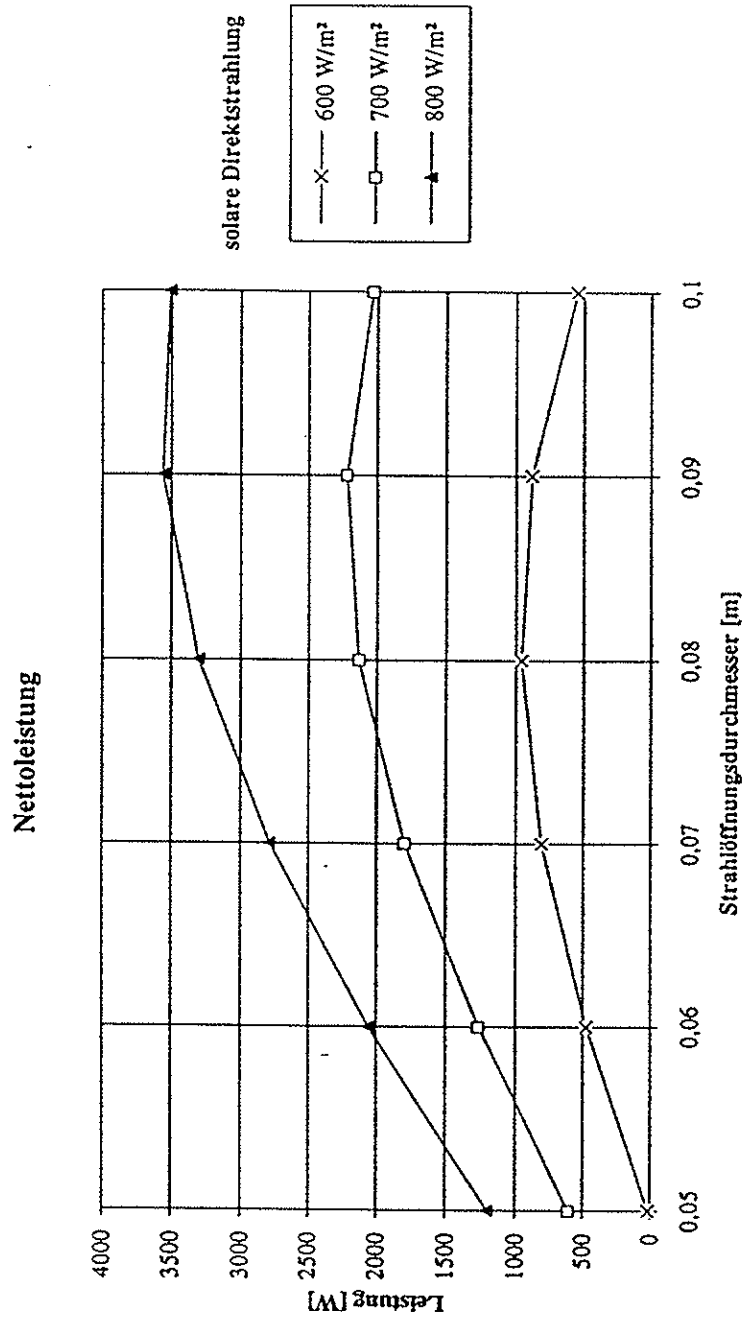


Bild 7: Nettoleistung in Abhängigkeit vom Öffnungsdurchmesser

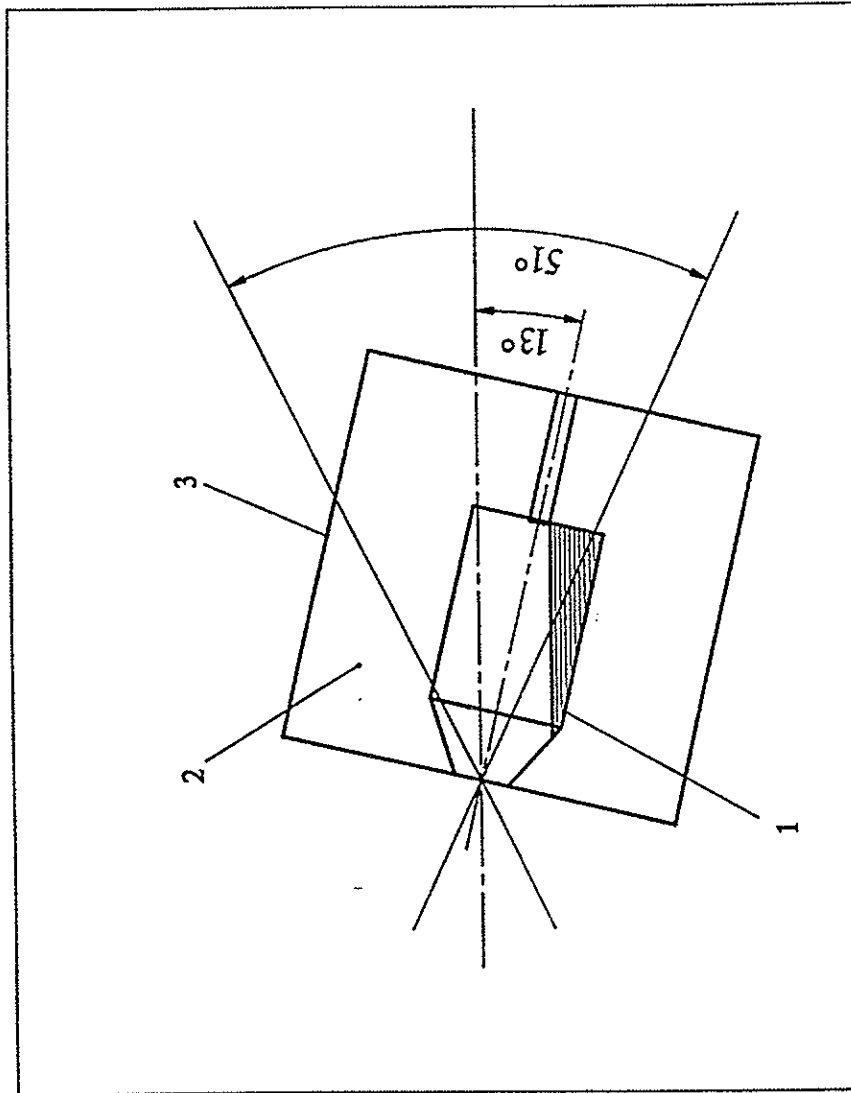


Bild 6: Reaktor in Betriebsstellung

High-Pressure Solar Ammonia Dissociation

Andreas Luzzi & Keith Lovergrove
 Australian National University (ANU)
 Department of Engineering
 Canberra, ACT 0200
 Australia

Though the reversible ammonia reaction $\text{NH}_3 + \Delta H \rightarrow 1/2\text{N}_2 + 3/2\text{H}_2$ might be termed Cinderella of solar thermochemistry due to its comparably small enthalpy of reaction of $\Delta H(30\text{MPa}) = 66.8 \text{ kJ/mol}$, it has the important advantages of:

- Total absence of side reactions,
- Spontaneous separation of components at ambient temperature, and
- Industrial expertise (NH_3, CH_4) with equipment that can be directly incorporated.

These factors contribute significantly to the prospect of design, operation as well as control simplicity of potential solar thermochemical power plants using ammonia.

ANU's ammonia research over two decades toward solar thermochemical power plants in a "distributed receiver/central power station" configuration include theoretical and experimental investigations of the important reaction kinetic and thermodynamic issues. Energy storage efficiency, exergetic optimisation and systems design as well as cost criteria have been studied theoretically. The existing experimental research facility comprises an ammonia laboratory for 1 kW_{chem} open and (soon completed) closed loop operation at up to 30 MPa and two paraboloidal solar concentrators with apertures of 20 m² and 400 m² respectively.

Both, electric-heater and solar-driven ammonia open loop dissociation experiments have been performed at pressures up to 15 MPa and power levels up to 2.5 kW_{chem}. The tubular reactors used feature annular cata-

lyst beds applying standard industrial catalysts (Ni-on- Al_2O_3 & promoted Fe/Co) and construction materials (Inconel 625 & 601).

The design and performance of such reactors have been simulated successfully with a combination of a two-dimensional pseudo-homogeneous numerical reactor model (NEWRE5), a 3D ray tracing code (COMPREC) and finite element stress / strain analyses (STRAND6). This led to the feasibility examination of possible full sized receiver / reactor concepts for the 20 m² dish and the 400 m² dish respectively.

The thermal time constant (50s) of the current directly-irradiated thick-walled tubular solar reactor opens the opportunity to test a convenient mass flow control strategy to run through solar transient conditions. The development of an adaptive flow rate control algorithm is on-going, aiming for energetic and exergetic optimisation of the endothermic ammonia dissociation reaction.

The recent completion of a detailed industry study on the feasibility of a 4 MWe solar assisted (distributed solar collector array of ANU's 400 m² dishes) natural gas base-load power plant for Tennant Creek, Northern Australia, encouraged a preliminary techno-economic investigation of replacing the direct-steam-generating solar facility (solar boiler & steam network) with a thermochemical ammonia system (reactor, network & ammonia boiler).

The presentation at PSI will summarise key-results of ANU's solar ammonia research.

High-Pressure Solar Ammonia Dissociation

● Introduction

- History of solar NH_3 research @ ANU → supported by slides

● ✓ Status Quo

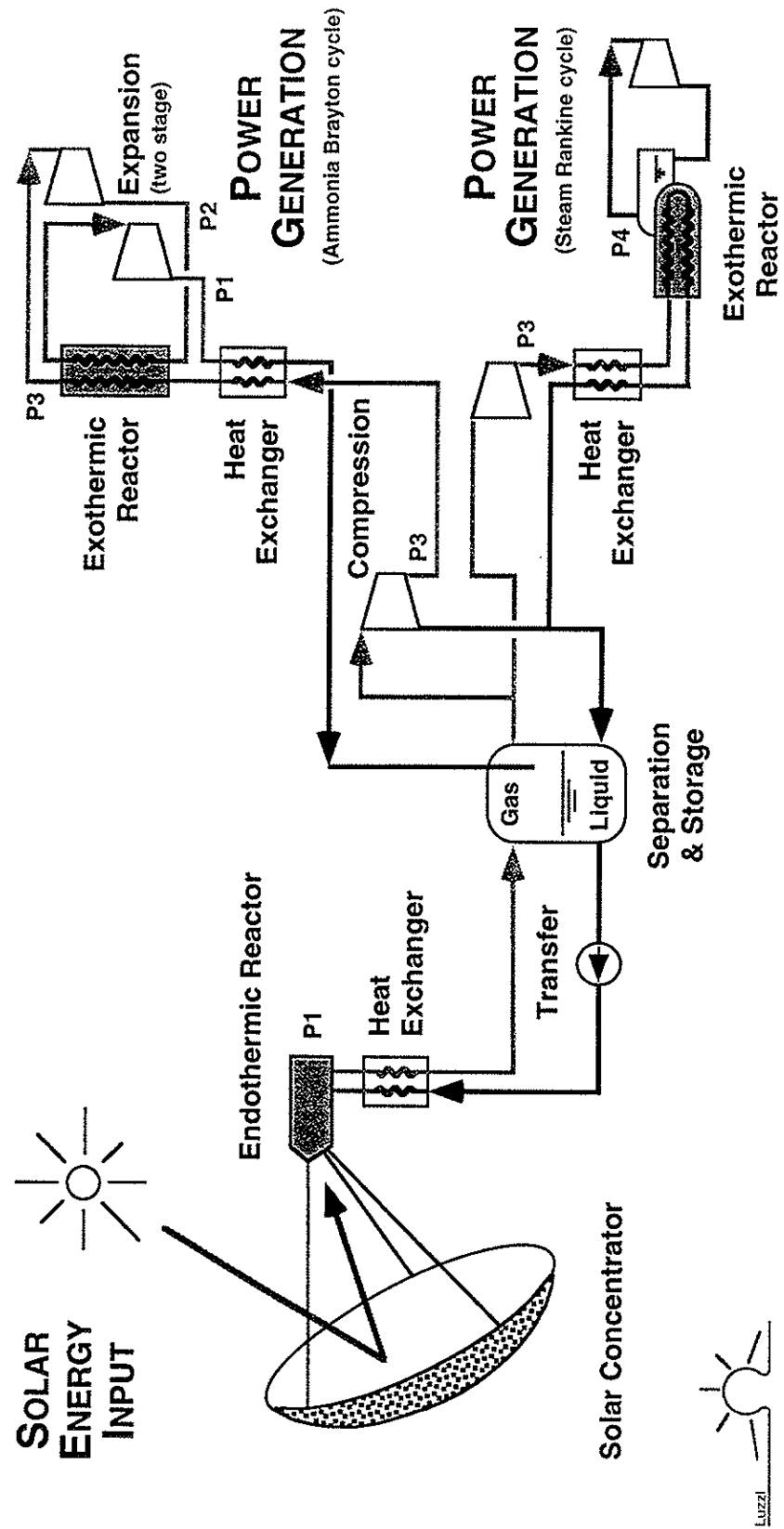
- Establishment of NH_3 laboratory, including 20m² dish
- Lab-scale 1kW_{chem} NH_3 dissociation experiments
- Validation of two-dimensional pseudo-homogeneous performance model (combined with 3D ray tracing software led to prediction with confidence)
- Prototype 1kW_{chem} solar ammonia dissociation reactor

○ Quo Vadis

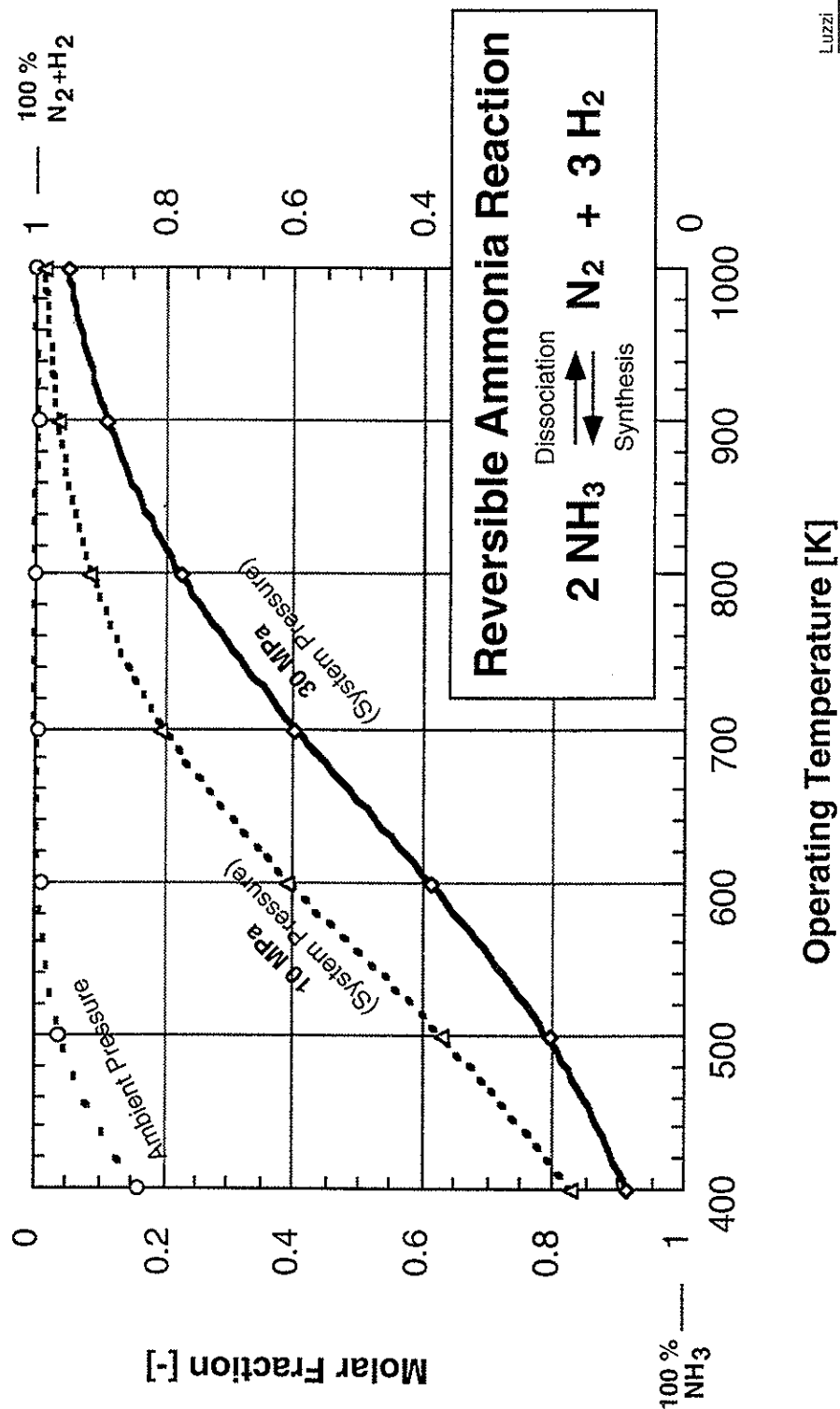
- Continuation of solar NH_3 dissociation experiments
- Assembly and testing of complete 1kW_{chem} closed-loop
- Implementation of reaction control strategy
- Exergetic (sub)-system optimisation studies
- Development of full-sized 15kW_{chem} reactor for 20m² dish
- Collaboration with NH_3 industry and power utilities

○ Slide Presentation

SOLAR THERMOCHEMICAL POWER GENERATION USING AMMONIA (BRAYTON OR RANKINE CYCLE)



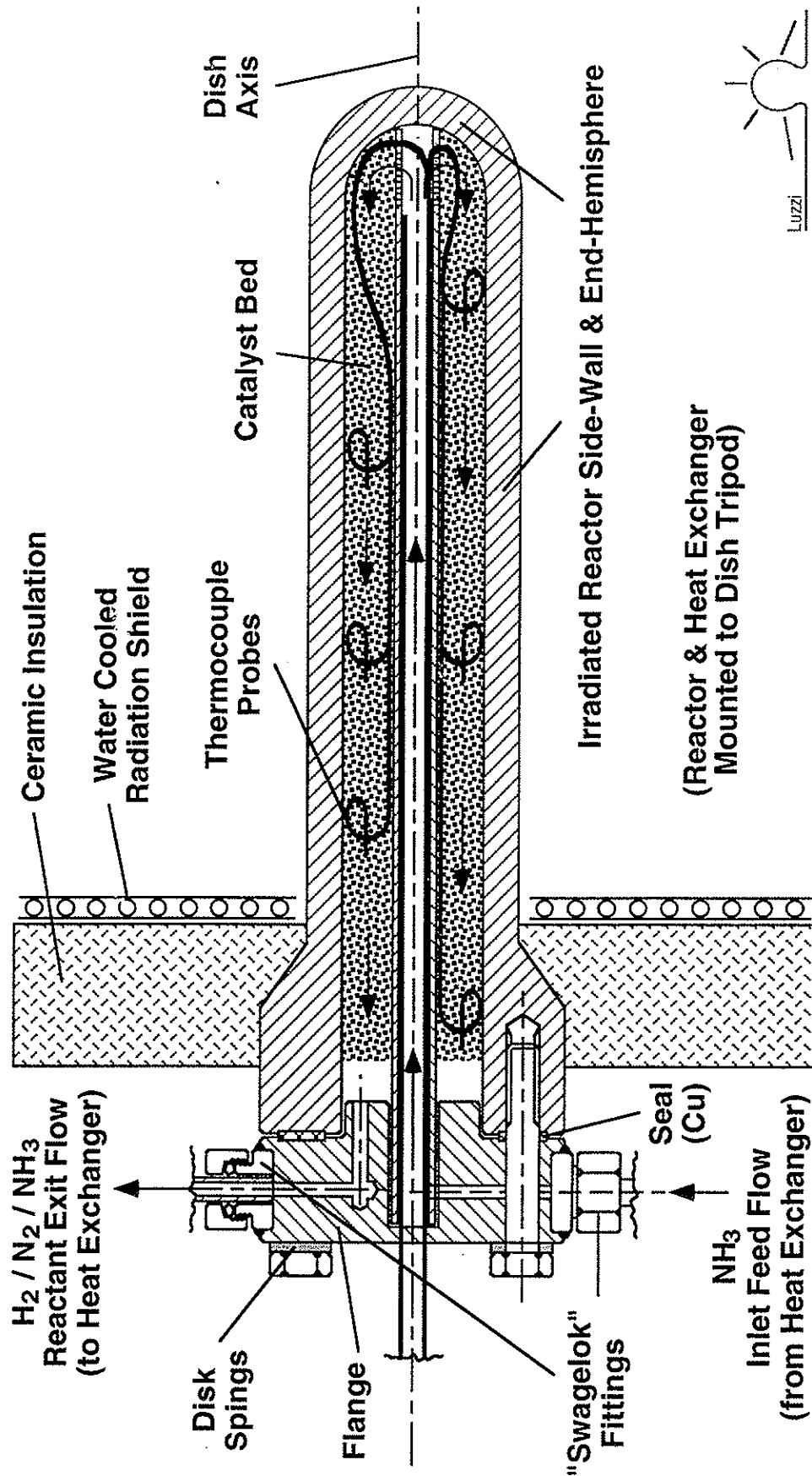
EQUILIBRIUM CURVE OF REVERSIBLE AMMONIA REACTION



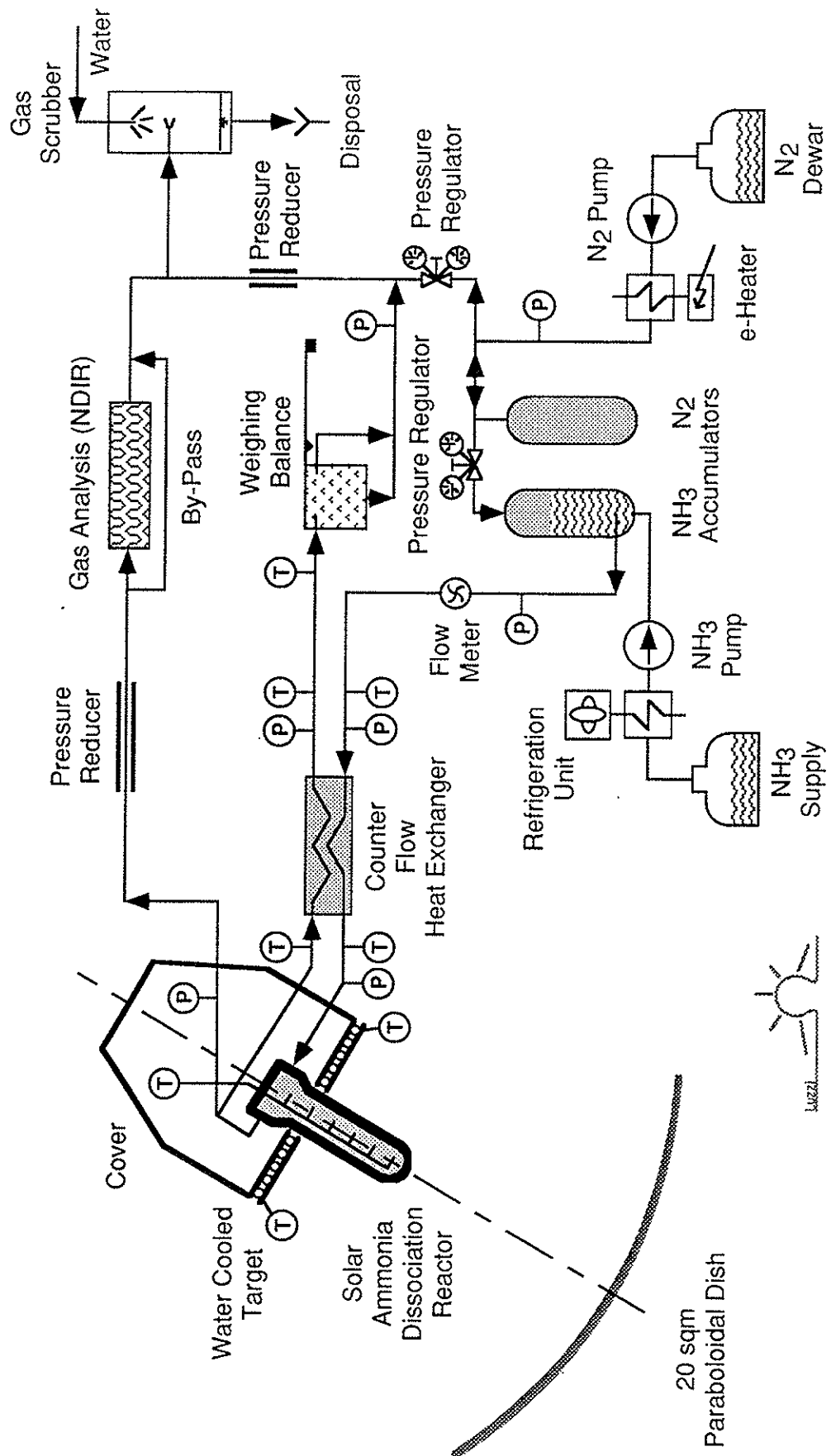
Luzzi

SOLAR AMMONIA RECEIVER / REACTOR

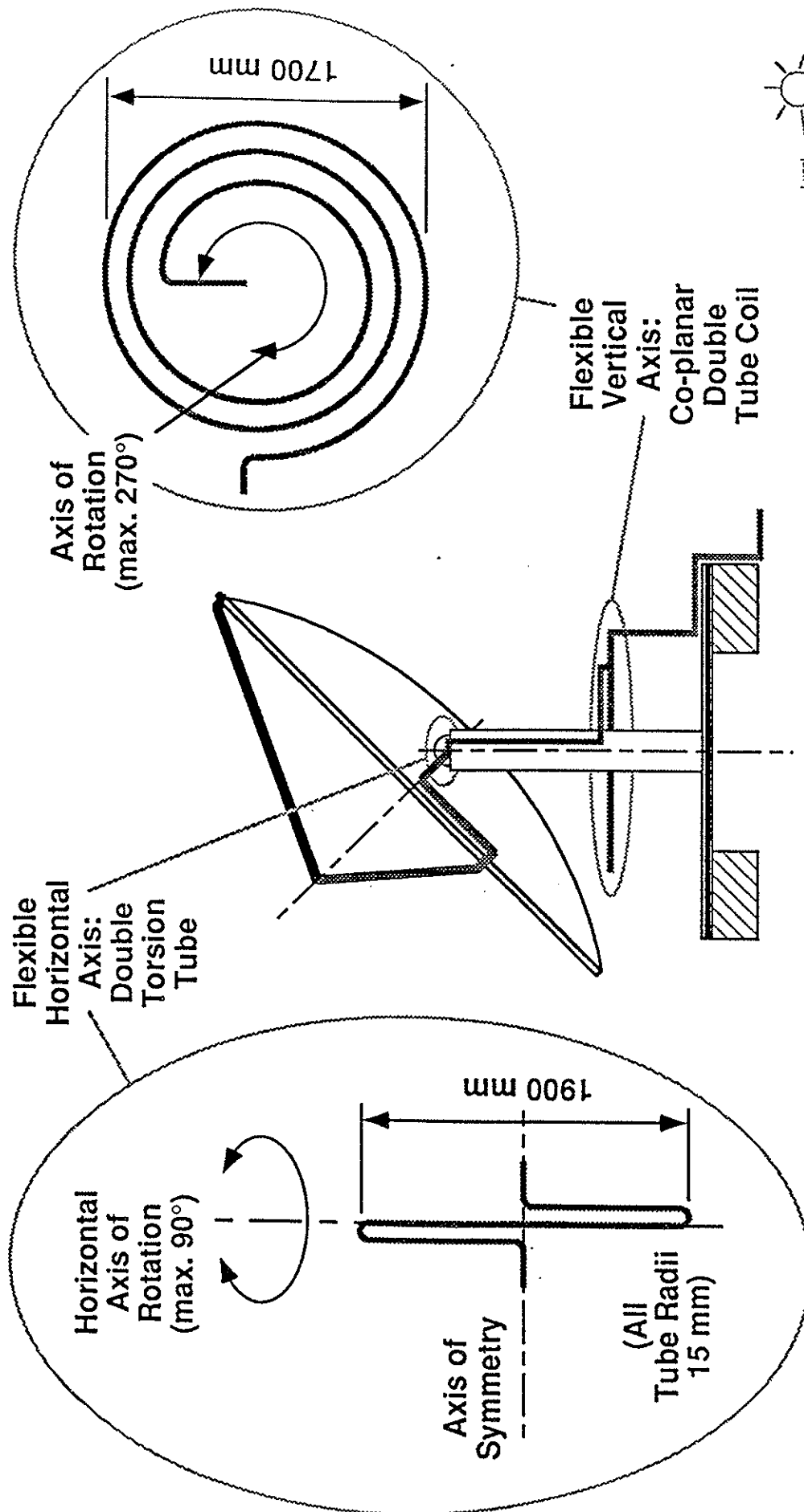
(Mk I)



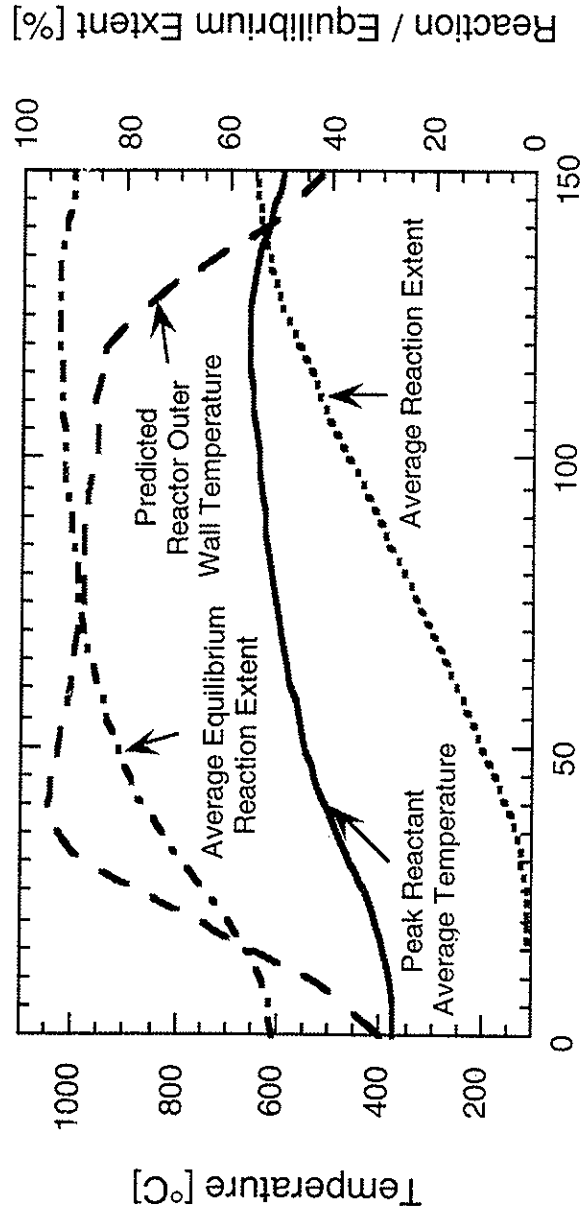
SCHEMATIC OF EXPERIMENTAL SOLAR AMMONIA DISSOCIATION SYSTEM



FLEXIBLE COUPLINGS 20MSQ DISH



EXPERIMENTALLY VERIFIED AXIAL PERFORMANCE PROFILES FOR 35MM OD SOLAR AMMONIA DISSOCIATION REACTOR

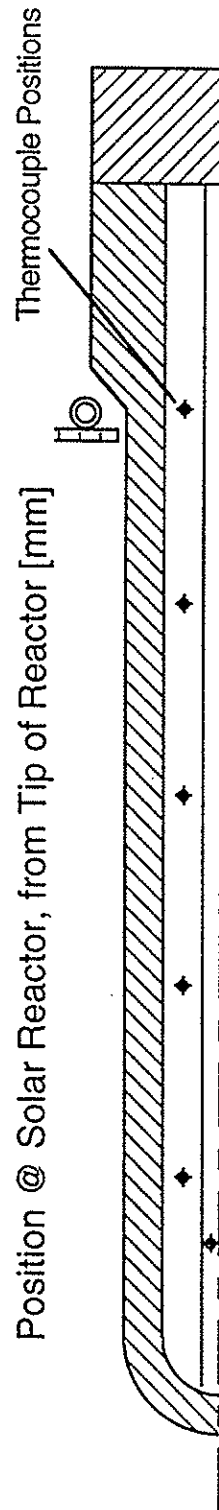
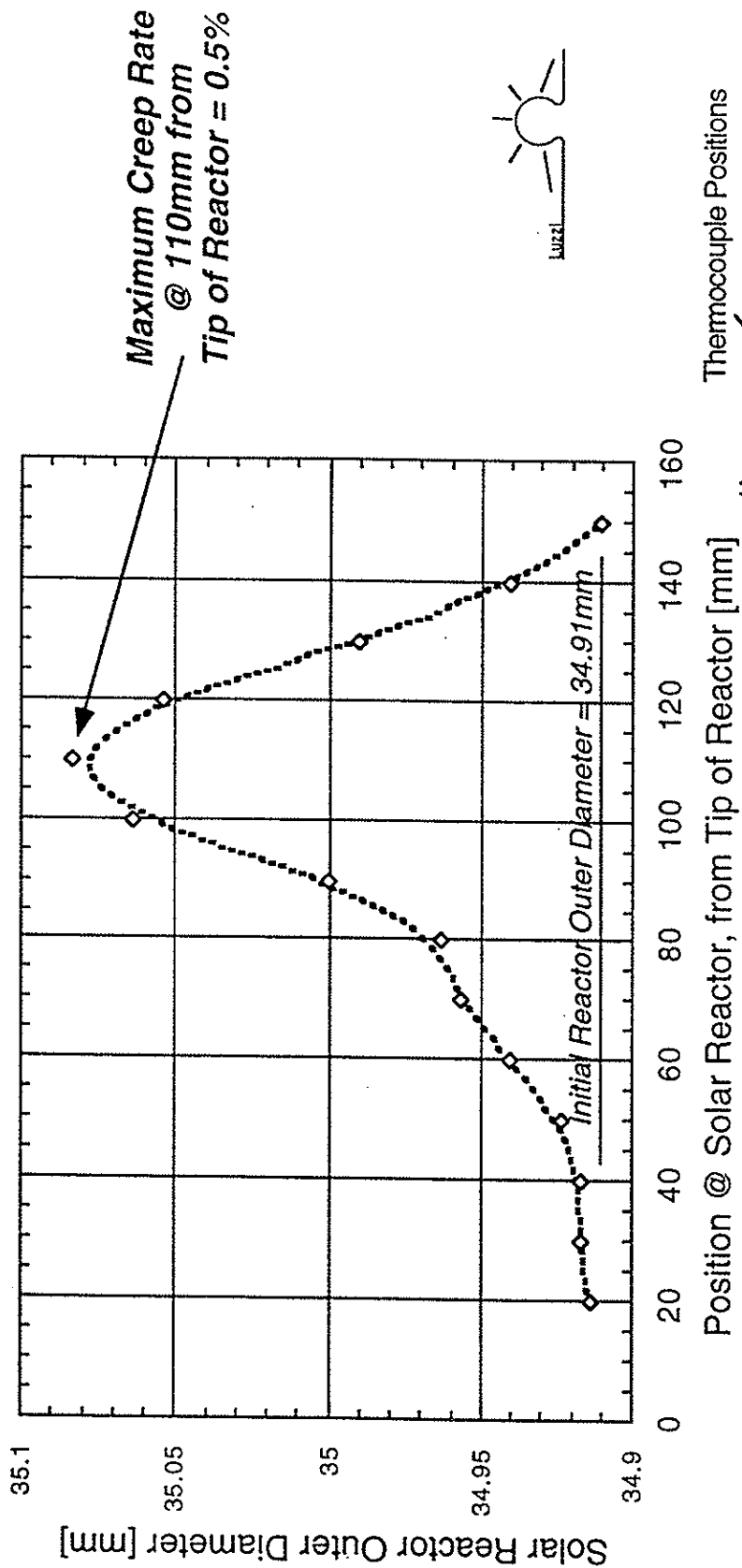


Axial Position Measured from Tip of Reactor [mm]

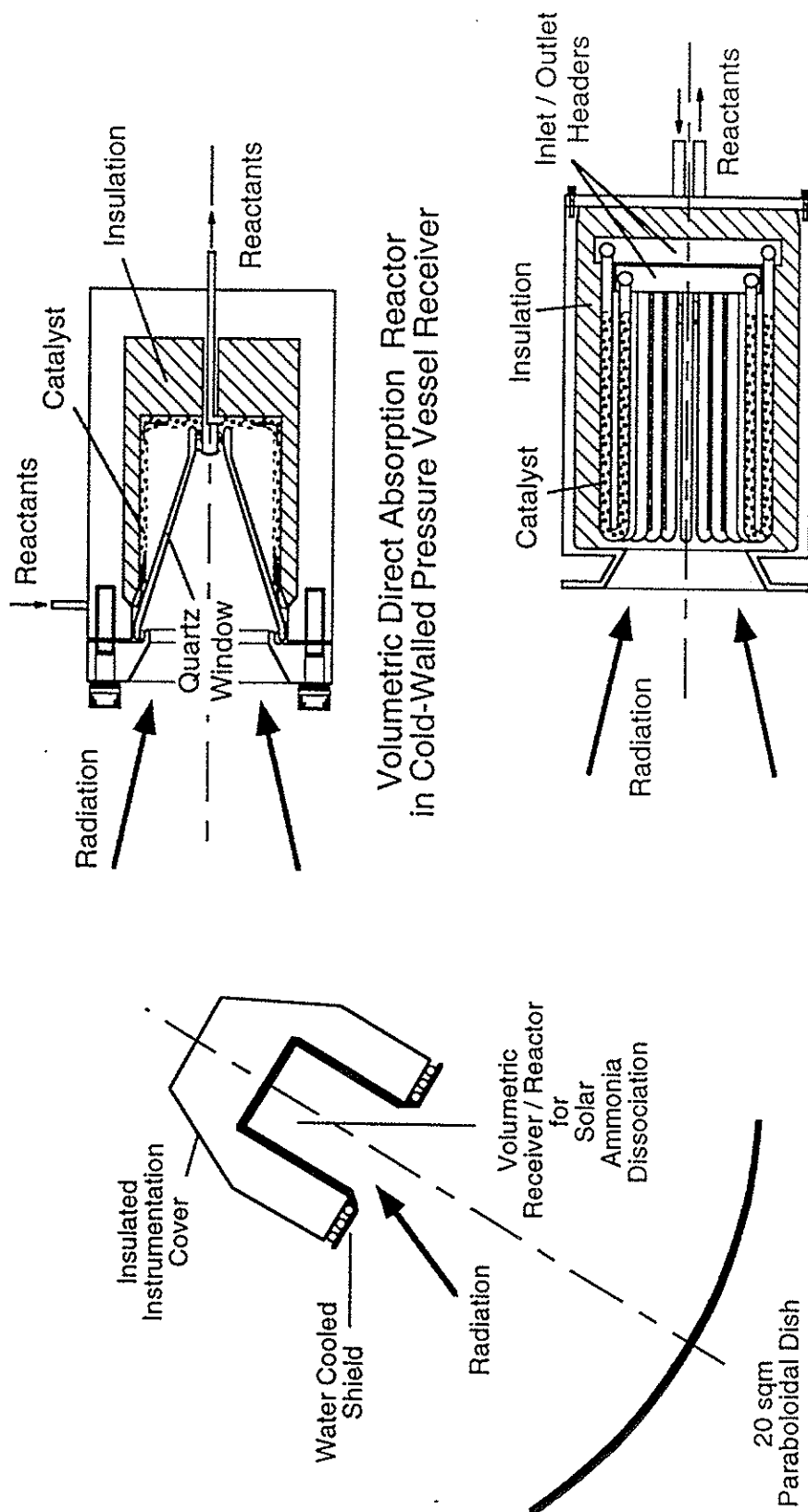


CREEP OF TUBULAR INCONEL 601 SOLAR AMMONIA REACTOR

(Measured 22 May 1995)



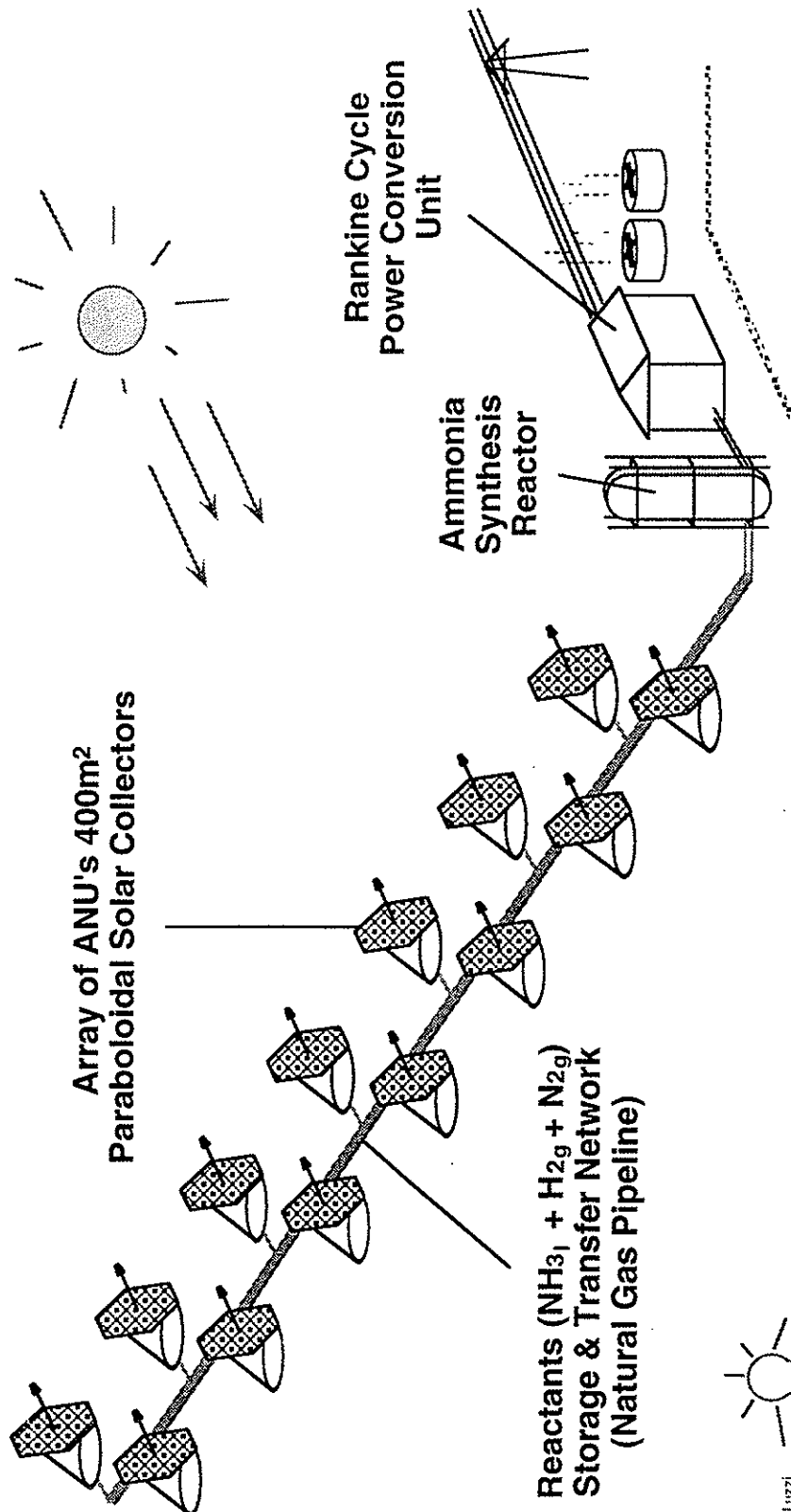
VOLUMETRIC RECEIVER / REACTOR CONCEPTS FOR AMMONIA DISSOCIATION USING 20SQM DISH



Cavity with Catalyst-Filled U-Tubes
Cylindrically Arranged in Insulated Receiver



SOLAR THERMOCHEMICAL POWER PLANT



Conclusions

Solar Ammonia Dissociation :

● ✓ Works

- *Its technical viability has been proven.*

● ✓ Is simple

- *High pressures are no impediment to cost effective reactor designs*
- *Standard catalysts + construction materials = excellent performance*
- *Flow rate control very appropriately manages endothermic reaction*

● ✓ Is predictive

- *Numerical model + ray tracing predict performance with confidence*

List of Participants

Australia

Mr. Andreas Luzzi
 Australian National University
 Department of Engineering
 CANBERRA ACT 0200
 Australia
 Tel. 0061 6 249 39 17
 Fax 0061 6 249 05 06
 luzzi@faceng.anu.edu.au

France

Dr. Jacques L    
 CNRS
 LSGC-ENSIC
 1 Rue Grandville, BP 451
 F-54001 NANCY
 France
 Tel. 0033 83 17 52 40
 Fax 0033 83 32 29 75

Germany

Dr. Karl-Heinz Funken
 Deutsche Forschungsanstalt f  r Luft- und
 Raumfahrt e.V. DLR
 MD-ET
 D-51140 K  LN
 Germany
 Tel. 0049 2203 606 32 20
 Fax 0049 2203 66 900

Mr. Thomas Hahm
 Universit  t Dortmund
 CT-AT
 D-44221 DORTMUND
 Germany
 Tel. 0049 231 755 25 99
 Fax 0049 231 755 23 41

Dr. J  rgen Ortner
 Deutsche Forschungsanstalt f  r Luft- und
 Raumfahrt e.V. DLR
 Solar Chemistry Section
 Linder H  he
 D-51147 K  LN
 Germany
 Tel. 0049 2203 601 27 66
 Fax 0049 2203 66 900

Prof. Armin Reller
 Universit  t Hamburg
 Inst. f  r Anorg. und Angew. Chemie
 Martin-Luther-King-Platz 6
 D-20146 HAMBURG
 Germany
 Tel. 0049 40 4123 3102
 Fax 0049 40 4123 6348

Prof. Henner Schmidt-Traub
 Universit  t Dortmund
 CT-AT
 D-44221 DORTMUND
 Germany
 Tel. 0049 231 755 23 38
 Fax 0049 231 755 23 41

Prof. Axel Sch  nbucher
 Gerhard-Mercator-Universit  t Duisburg
 Kommandantenstr. 60
 D-47048 DUISBURG
 Germany
 Tel. 0049 203 3789 220
 Fax 0049 203 3789 351

Mr. Zaharias Veziridis
 Degussa Ag
 Zentrale Forschungseinrichtung
 Postfach 1345
 D-63403 HANAU
 Germany
 Tel. 0049 61 81 59 45 13
 Fax 0049 61 81 59 35 54

Israel

Dr. Michael Epstein
 Weizmann Institute of Science
 P.O. Box
 76100 REHOVOT
 Israel
 Tel. 009 728 343 804
 Fax 009 728 344 117

Japan

Prof. Yutaka Tamaura
 Research Center for Carbon Recycling &
 Utilization
 Tokyo Institute of Technology
 Ookayama, Meguro-ku
 TOKYO 152
 Japan
 Tel. 0081 3 5734 32 92
 Fax 0081 3 5734 32 92 or 34 36

Prof. Masamichi Tsuji
Research Center for Carbon Recycling &
Utilization
Tokyo Institute of Technology
Ookayama, Meguro-ku
TOKYO 152
Japan
Tel. 0081 3 5734 33 37
Fax 0081 3 5734 33 37

Switzerland

Mr. Olav Becker
Paul Scherrer Institut
Solarchemie
38/311
CH-5232 VILLIGEN PSI
Switzerland
Tel. 0041 56 310 24 29
Fax 0041 56 310 21 99

Mr. Max Brack
Paul Scherrer Institut
Solare Verfahrenstechnik
162/4
CH-5232 VILLIGEN PSI
Switzerland
Tel. 0041 56 310 27 93
Fax 0041 56 310 21 99

Dr. Christophe De Reyff
Swiss Federal Office of Energy
CH-3003 BERN
Switzerland
Tel. 0041 31 322 56 66
Fax 0041 31 382 44 03

Dr. Koebi Ehrensberger
Paul Scherrer Institut
Solarchemie
104/1
CH-5232 VILLIGEN PSI
Switzerland
Tel. 0041 56 310 40 79
Fax 0041 56 310 44 13

Dr. Baldur Eliasson
ABB Management Ltd.
Corporate Research
Segelhof
Postfach
CH-5405 BADEN-DÄTTWIL
Switzerland
Tel. 0041 56 76 80 31
Fax 0041 56 83 45 69

Mr. Jorge Ferreira
ETH Zentrum
Lab. für Energiesysteme
CH-8092 ZÜRICH
Switzerland
Tel. 0041 1 632 69 15
Fax 0041 1 632 10 23

Mr. Martin Forster
Cerberus AG
CH-8708 MÄNNEDORF
Switzerland
Tel. 0041 1 922 61 11
Fax 0041 1 922 64 50

Mr. Alwin Frei
Paul Scherrer Institut
Solarchemie
38/311
CH-5232 VILLIGEN PSI
Switzerland
Tel. 0041 56 310 43 02
Fax 0041 56 310 21 99

Mr. Hans Fricker
FC Consulting
Breiteststr. 22
CH-8544 RICKENBACH
Switzerland
Tel. 0041 52 37 17 48
Fax 0041 52 37 15 62

Mr. Jochen Ganz
Paul Scherrer Institut
Solare Verfahrenstechnik
104/2
CH-5232 VILLIGEN PSI
Switzerland
Tel. 0041 56 310 40 64
Fax 0041 56 310 44 13

Dr. Otto Haas
Paul Scherrer Institut
Elektrochemie
38/123
CH-5232 VILLIGEN PSI
Switzerland
Tel. 0041 56 310 24 72
Fax 0041 56 310 44 15

Mr. Philipp Haueter
 Paul Scherrer Institut
 Solare Verfahrenstechnik
 VT-Halle
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 27 96
 Fax 0041 56 310 21 99

Dr. Bernd Hemmerling
 Paul Scherrer Institut
 Verbrennungsdiagnostik
 21/113
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 24 76
 Fax 0041 56 310 21 99

Dr. James Highfield
 Paul Scherrer Institut
 Katalyse
 21/115
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 20 60
 Fax 0041 56 310 21 99

Dr. Stefan Hirschberg
 Paul Scherrer Institut
 21/316
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 29 56
 Fax 0041 56 310 21 99

Ms. Franziska Holzer
 Paul Scherrer Institut
 Elektrochemie
 38/121
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 40 96
 Fax 0041 56 310 44 15

Dr. Paul Hug
 UNI Zürich
 Anorg. Chem. Institut
 Winterthurerstr. 190
 CH-8057 ZÜRICH
 Switzerland
 Tel. 0041 1 257 46 78
 Fax 0041 1 363 86 11

Mr. Arthur Imhof
 Paul Scherrer Institut
 Solare Verfahrenstechnik
 162/1
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 37 22
 Fax 0041 56 310 21 99

Dr. Aldo Jakob
 Paul Scherrer Institut
 Stoffkreisläufe
 21/111
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 26 96
 Fax 0041 56 310 21 99

Mr. Martin Jakob
 Paul Scherrer Institut
 Energiemodelle
 106/19
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 41 68
 Fax 0041 56 310 44 12

Dr. Ivo Kamber
 Paul Scherrer Institut
 Solarchemie
 104/4
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 40 92
 Fax 0041 56 310 44 13

Dr. Paul Kesselring
 Paul Scherrer Institut
 Allgemeine Energieforschung
 21/202
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 27 23
 Fax 0041 56 310 44 16

Dr. Helmut Kiess
 Paul Scherrer Institut
 154/2
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 37 53
 Fax 0041 56 310 21 99

Dr. Jürgen Kritzenberger
Paul Scherrer Institut
Energiespeicherung
6c/P104
CH-5232 VILLIGEN PSI
Switzerland
Tel. 0041 56 310 40 16
Fax 0041 56 310 21 99

Dr. Peter Kuhn
Paul Scherrer Institut
Solarchemie
104/3
CH-5232 VILLIGEN PSI
Switzerland
Tel. 0041 56 310 20 74
Fax 0041 56 310 44 13

Dr. Anton Meier
Paul Scherrer Institut
Solare Verfahrenstechnik
162/2
CH-5232 VILLIGEN PSI
Switzerland
Tel. 0041 56 310 27 88
Fax 0041 56 310 21 99

Mr. Stefan Menzi
ETH Zürich
Mess- und Regeltechnik
CH-8092 ZÜRICH
Switzerland
Tel. 0041 1 632 24 69
Fax

Mr. Christoph A. Mikšovic
ETH Zentrum
Lab. für Energiesysteme
IES-LES
CH-8092 ZÜRICH
Switzerland
Tel. 0041 1 632 78 58
Fax 0041 1 632 11 76

Dr. Daniel Mischler
Paul Scherrer Institut
Solare Verfahrenstechnik
162/1
CH-5232 VILLIGEN PSI
Switzerland
Tel. 0041 56 310 27 95
Fax 0041 56 310 21 99

Prof. Peter Oelhafen
Uni Basel
Institut für Physik
CH-4056 BASEL
Switzerland
Tel. 0041 61 267 37 13
Fax 0041 61 267 37 84

Prof. H.R. Oswald
Uni Zürich
Anorg. Chem. Institut
Winterthurerstr. 190
CH-8057 ZÜRICH
Switzerland
Tel. 0041 1 257 46 11
Fax 0041 1 363 86 11

Mr. Thomas Pykkänen
Atlantis Energie AG
Lindenrain 4
CH-3012 BERN
Switzerland
Tel. 0041 31 300 32 20
Fax 0041 31 300 32 30

Mrs. Manuela Quintilii
Paul Scherrer Institut
38/219
CH-5232 VILLIGEN PSI
Switzerland
Tel. 0041 56 310 26 15
Fax 0041 56 310 21 99

Dr. Claude Revilliod
EPFL
IC P2
CH-1015 LAUSANNE
Switzerland
Tel. 0041 21 693 31 08
Fax 0041 21 693 41 11

Dr. Harald Ries
Paul Scherrer Institut
Solarchemie
104/5
CH-5232 VILLIGEN PSI
Switzerland
Tel. 0041 56 310 29 61
Fax 0041 56 310 44 13

Mr. Franz Saladin
 Paul Scherrer Institut
 Solarchemie
 38/311
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 41 95
 Fax 0041 56 310 21 99

Mr. Thomas Schelling
 Paul Scherrer Institut
 Solare Verfahrenstechnik
 162/3
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 29 61
 Fax 0041 56 310 21 99

Dr. Günther G. Scherer
 Paul Scherrer Institut
 Brennstoffzellen
 38/113
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 23 62
 Fax 0041 56 310 44 15

Dr. Markus Schubnell
 Paul Scherrer Institut
 Solarchemie
 104/5
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 27 97
 Fax 0041 56 310 44 13

Mr. Thomas Seitz
 Paul Scherrer Institut
 Solare Verfahrenstechnik
 VT-Halle
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 29 79
 Fax 0041 56 310 21 99

Dr. Valery Shklover
 ETH Zentrum
 Lab. of Crystallography
 CH-8092 ZÜRICH
 Switzerland
 Tel. 0041 1 632 37 35
 Fax 0041 1 632 11 33

Mr. Eugen Steiner
 Paul Scherrer Institut
 Solarchemie
 104/2
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 27 92
 Fax 0041 56 310 44 13

Dr. Aldo Steinfeld
 Paul Scherrer Institut
 Solare Verfahrenstechnik
 162/1
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 29 78
 Fax 0041 56 310 21 99

Dr. Samuel Stucki
 Paul Scherrer Institut
 Stoffkreisläufe
 21/112
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 41 54
 Fax 0041 56 310 21 99

Prof. Peter Suter
 ETH Zentrum
 Lab. für Energiesysteme
 CH-8092 ZÜRICH
 Switzerland
 Tel. 0041 1 632 27 32
 Fax 0041 1 632 11 76

Mr. Fritz von Roth
 Paul Scherrer Institut
 Wasserstoffspeicherung
 21/115
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 41 32
 Fax 0041 56 310 21 99

Mrs. Claudia von Scala
 Paul Scherrer Institut
 Energiespeicherung
 21/114
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 29 23
 Fax 0041 56 310 21 99

Dr. Erich Wieland
 Paul Scherrer Institut
 108/409/B
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 22 91
 Fax 0041 56 310 21 99

Ms. Anke Weidenkaff
 Paul Scherrer Institut
 Solarchemie
 38/311
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 24 29
 Fax 0041 56 310 21 99

Prof. Alexander Wokaun
 Paul Scherrer Institut
 Allgemeine Energieforschung
 21/210
 CH-5232 VILLIGEN PSI
 Switzerland
 Tel. 0041 56 310 27 51
 Fax 0041 56 310 44 16

United States of America

Dr. Daniel M. Blake
 NREL
 1617 Cole Blvd.
 GOLDEN, CO 80401-3393
 USA
 Tel. 001 303 275 3702
 Fax 001 303 275 3896

Prof. Edward A. Fletcher
 University of Minnesota
 III Church St. S.E.
 Mechanical Engineering
 MINNEAPOLIS, MINNESOTA 55455
 USA
 Tel. 001 612 625 0532
 Fax 001 612 624 1398

Prof. Jean P. Murray
 Portland State University
 P.O. Box 751
 PORTLAND OR 97207-0751
 USA
 Tel. 001 503 725 3814
 Fax 001 503 725 4298

Mrs. Carol Palumbo
 Valparaiso University
 Mechanical Engineering
 VALPARAISO IN 46383
 USA
 Tel. 001 219 464 5135
 Fax 001 219 464 5065

Prof. Robert Palumbo
 Valparaiso University
 Mechanical Engineering
 VALPARAISO IN 46383
 USA
 Tel. 001 219 464 5135
 Fax 001 219 464 5065

