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THERMOCHEMICAL AND RADIATION CHEMICAL
HYDROGEN PRODUCTION

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and Hayato NAKAJIMA

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Thermochemical and Radiation Chemical Hydrogen Production

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In search of closed-cycle hydrogen production processes by nuclear energy, thermochemical and radiation chemical reactions have been studied which are related to candidate processes.

In a hopeful thermochemical process, nickel, iodine and sulfur are used (NIS process). This process is an improved iodine-sulfur process, and is characterized by the separation of nickel iodide and sulfate by solvent extraction and the high temperature decomposition of sulfur trioxide in the absence of water. Experimental results of main unit operations are described. Another feasible process with carbon dioxide was also studied using ferrous iodide.

For radiation chemical hydrogen production, radiolysis of carbon dioxide was studied by gamma-rays and reactor radiations containing fission fragments, and with nitrogen dioxide and propane as additives. The mechanism of reoxidation of carbon monoxide, the back reaction, is discussed, because the back reaction determines the carbon monoxide yield.

Keywords: Hydrogen Production, Closed-Cycle Process, Thermochemical Process, Radiation Chemical Process, Sulfur, Iodine, Nickel, Ferrous Iodide, Carbon Dioxide, Carbon Monoxide, Gamma-Rays, Fission Fragments.

熱化学的および放射線化学的水素製造

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(1979年9月20日受理)

核エネルギーによる閉サイクル水素製造法の探索を行い、熱化学的および放射線化学的プロセスとして適当と思われる反応を研究した。

熱化学プロセスの研究では、沃素・硫黄プロセスの改良法に相当する、ニッケル・沃素・硫黄を用いるプロセス(NISプロセス)を研究した。このプロセスは、沃化ニッケルと硫酸ニッケルを溶媒抽出により分離する点と、最高温反応で水を含まない三酸化硫黄熱分解反応を行う点に特徴がある。主要な単位操作についての実験結果について述べた。また、炭酸ガスを用いるプロセスとしては、沃化鉄を用いる実行可能なプロセスを見出した。

放射線化学プロセスの研究では、添加物として二酸化窒素とプロパン、また放射線として核分裂片を含む炉内放射線とガンマ線を用いて、炭酸ガスの分解を行った。一酸化炭素収率に影響の大きい、逆反応(一酸化炭素の再酸化)の機構について議論した。

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1. Introduction

Nuclear energy can be utilized for hydrogen production in the form of either heat or radiations.

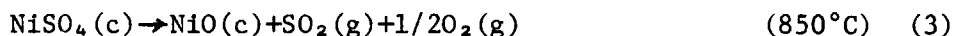
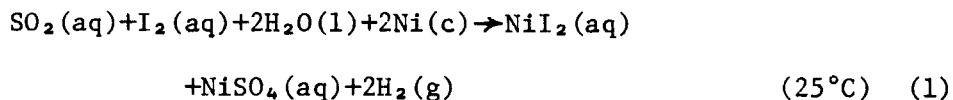
The heat required in the thermochemical process for the hydrogen production is expected to be supplied from the high temperature gas-cooled reactor (HTGR). An experimental HTGR for process heat applications is under study by Japan Atomic Energy Research Institute. The reactor construction is scheduled to be completed in the later '80s. The maximum process temperature of 850 to 900°C will become available. Possible chemical reactions to be included in the thermochemical processes have been studied and two processes, NIS process and CO₂ process are found chemically feasible.

Radiation energies for radiation chemical processes may be obtained from a nuclear fission or fusion reactor, high level radioactive wastes, or an accelerator, if economics permitted. Radiolysis of carbon dioxide has been studied, because the reaction may be an efficient conversion process of radiation energy to chemical energy.

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2. NIS Process

NIS process is composed of the reactions of nickel, iodine, and sulfur oxides,



The iodine-sulfur cycle has been studied extensively, and many variations have been proposed.¹⁻⁴⁾ NIS process is one of them.

Reaction 1 proceeds spontaneously at room temperature, and hydrogen of high purity, more than 97 %, was generated. After reaction 1, nickel iodide is separated from nickel sulfate by solvent extraction. Each nickel salt is pyrolyzed according to reaction 2 or 3. Reaction 3 requires the highest temperature, 850°C, in the NIS process. This temperature corresponds to the maximum available temperature from the high temperature reactor. It may be desirable from the viewpoint of nuclear reactor safety that hydrogen does not take part in the high temperature reactions of the thermochemical processes. If hydrogen were present, it would permeate easily through the metallic wall of the heat exchanger at high temperature, and contaminate the coolant helium in the nuclear reactor circuits. A half of hydrogen generated in reaction 1 is used to reduce nickel oxide in reaction 4.

2.1 Hydrogen evolution

Fig. 1 shows hydrogen evolution by reaction 1. Mixed acid, i.e., mixture of sulfuric and hydroiodic acid, was formed first by introducing sulfur dioxide to aqueous suspension of iodine. Next, nickel

metal powder was added to the mixed acid. Thermal efficiency of this process depends strongly on the concentration of the mixed acid. The highest concentration of the mixed acid obtainable, without side reaction to form free sulfur, was 35 w/o HI + 13 w/o H_2SO_4 at about $60^\circ C$. At this temperature, reagent nickel powder was added to the mixed acid. Hydrogen yield was more than 95 % of the calculated value at the reaction time of 60 minutes. The purity of hydrogen was higher than 97 % by gaschromatography.

2.2 Separation of mixed nickel salts

Nickel iodide and nickel sulfate formed in reaction 1, must be separated before their pyrolysis. Several methods seem possible for their separation. We adopted ethanol extraction method. The solubilities of nickel iodide and nickel sulfate in ethanol are shown in Table 1. Nickel iodide has high solubility in ethanol, but nickel sulfate does not dissolve in ethanol practically.

Fig. 2 shows extraction of nickel iodide from dehydrated mixed nickel salts by ethanol. For the extraction, 0.04 moles each of nickel iodide and nickel sulfate, and 0.4 moles of ethanol were used at $60^\circ C$. Ethanol solution was stirred by a magnetic stirrer. 83 % of nickel iodide was extracted at the extraction time of 60 minutes.

2.3 Pyrolysis of nickel salts

Pyrolysis of nickel iodide and nickel sulfate was studied by thermogravimetry, as shown in Fig. 3. Nickel iodide started to decompose at about $500^\circ C$, and nickel metal sponge was obtained at about $650^\circ C$.

Decomposition of nickel sulfate took place at a higher temperature. The higher the rate of temperature raise, the higher the end point of reaction. Pure nickel oxide was obtained below 900°C. Similar decomposition curves of nickel sulfate were obtained in both air and argon atmosphere.

2.4 Reduction of nickel oxide

Nickel oxide formed by the pyrolysis of nickel sulfate is reduced to nickel by hydrogen (Fig. 4). For the reduction, 3.5 g of nickel oxide was used in the hydrogen stream of 30 ml/min at 400°C. The reaction was nearly complete after 5 hours.

2.5 Flowsheet

A simplified flow sheet of the NIS process is shown in Fig. 5. One mole of water is supplied to the process, and one mole of hydrogen and a half mole of oxygen are obtained. In addition to chemical reactions, 1, 2, 3, and 4, accompanying operations such as dehydration, extraction, and ethanol evaporation are necessary.

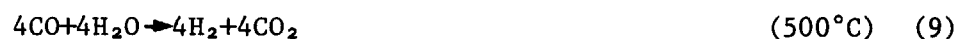
Heat balance was calculated for this flowsheet, as shown in Table 2. A total of about 2500 kJ heat must be supplied for the decomposition of one mole of water. Out of this, about 1300 kJ is needed for the dehydration step, which is below 300°C, and 600 kJ for the ethanol evaporation step, which is below 150°C. This means that, in this process, a large amount of heat is needed at relatively low temperature.

The thermal efficiency of this process was estimated to be 30 - 40 % on the basis of this preliminary flowsheet, when 70 - 80 % heat recovery was assumed. Possible optimization of the process is under study.

3. CO₂ Process

The second thermochemical process studied is characterized by decomposition of carbon dioxide. Decomposition of carbon dioxide was attempted, considering that handling of hydrogen at high temperature could be avoided and that problems of reactor materials may be reduced, compared with that of water decomposition at high temperature.⁵⁻⁷⁾ Decomposition of carbon dioxide was studied by the reaction with transition metal halides.

A typical process with carbon dioxide (II-J process) is composed of the following reactions,



Carbon dioxide reacts with ferrous iodide, and carbon monoxide is obtained (reaction 5). Magnetite thus formed is reduced to ferrous iodide by the reaction with gaseous hydrogen iodide, without ferric products. Reactions 7 and 8 are known reactions. A closed cycle of carbon dioxide decomposition is composed by reactions 5, 6, 7, and 8. Combining them with the water shift reaction 9, a closed cycle of water decomposition is obtained. In this process, reaction 5 requires the highest temperature.

3.1 Reaction of carbon dioxide with ferrous halides

Reactions of carbon dioxide with ferrous halides were examined, and carbon monoxide was formed as shown in Fig. 6. When carbon dioxide reacted with ferrous iodide at one atmospheric, carbon mono-

xide concentration in carbon dioxide stream reached 20 % at 900°C. Lower concentrations of carbon monoxide were obtained for the reaction with ferrous bromide or ferrous chloride. Ferrous iodide is the most promising for the decomposition of carbon dioxide. By this reaction, ferrous iodide is converted completely to magnetite.

3.2 Reaction of magnetite with hydrogen halides

Reactions of magnetite with hydrogen halides were examined, and the reduction of magnetite to ferrous halide is shown in Table 3. At 200°C, magnetite was completely reduced to ferrous iodide by gaseous hydrogen iodide, while the products were mixtures of ferrous and ferric halides by the reaction with hydrogen bromide or chloride.

From these experiments, a few processes with carbon dioxide and ferrous halides could be formulated. The most promising was the II-J process shown before. All the reactions in this process proceeded with high reaction rates, but some difficulties are foreseen in the separation of reaction products.

4. Radiolysis of Carbon Dioxide

Compared with thermal reactions, radiation chemical reactions have a characteristic of not being dictated by thermal equilibrium. So the reactions are controlled by the primary activation process of ionizing radiations, and by reaction rates of active species formed by radiations. Another feature of the radiation chemical reaction is that ionic species play important roles in the reaction mechanism.

Combined with water shift reaction 9, radiolysis of carbon dioxide 10 constitutes a closed cycle of water decomposition.



Radiation energy can be converted to chemical energy effectively by

the radiolysis of carbon dioxide.⁸⁾ The energy sources can be the high level radioactive wastes, the nuclear fission reactors or possibly the fusion reactors in the future.

One problem with this radiolysis is that carbon monoxide formed during the reaction is easily reoxidized to carbon dioxide by a rapid back reaction.⁹⁾ This back reaction is a main factor to lower the carbon monoxide yield and energy conversion efficiency. Some ionic species might be involved in the back reaction, but their effects on the mechanism of the back reaction has not been clarified yet. A basic research was made to investigate the reaction.

4.1 Back reaction

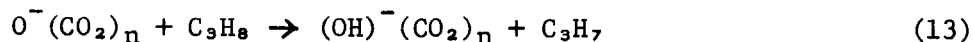
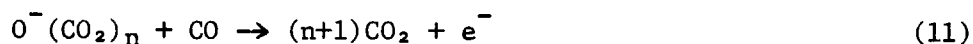
The back reaction was studied by addition of propane to carbon dioxide (Fig. 7). With pure carbon dioxide, the carbon monoxide yield was zero because of the rapid back reaction. At 0.5 % propane, the back reaction was completely suppressed by the scavenging effect of propane, and carbon monoxide yield reached 4.5 in G value. Between 0 and 0.5 % propane, the back reaction was investigated further.

Pressure dependence of carbon monoxide yield is shown in Fig. 8. When the back reaction was suppressed by high concentration propane, carbon monoxide yield was independent of the total pressure. In contrast, when the back reaction was partially suppressed, carbon monoxide yield decreased with pressure raised. This result shows that the back reaction is accelerated at high pressure.

4.2 Mechanism of back reaction

The back reaction was investigated also in terms of temperature and dose rate.¹⁰⁾ The analysis of the results gave the following

mechanism of back reaction.



The oxidizing species is an $O^-(CO_2)_n$ ion. It oxidizes carbon monoxide. At high dose rates, it recombines with a cation, R^+ , and the back reaction is retarded. This mechanism gives some hints to improve the carbon monoxide yield. The first is that the yield will increase by the irradiation of high LET radiations, such as fission fragments. The second is that additives must have a high reactivity with the negative ion, $O^-(CO_2)_n$.

4.3 Fission fragment radiolysis

Fission fragments have an extremely high LET value, and radiolysis thereby may have a different energy conversion efficiency to that by gamma-rays. Carbon monoxide yields from the carbon dioxide - propane system by fission fragments or gamma-rays are shown in Fig. 9. When propane concentration was 1 %, a maximum carbon monoxide concentration of 0.8 % was obtained by gamma-ray irradiation. By fission fragment irradiation, carbon monoxide concentration increased to about 2 %, and the G-value by fission fragments was greater than that by gamma-rays.

4.4 Nitrogen dioxide addition

Fig. 10 shows the yields of carbon monoxide and oxygen with the addition of nitrogen dioxide instead of propane. When 1 % nitrogen dioxide was added, carbon monoxide concentration was more than 4 %, and oxygen concentration about 2 % at an exposure of 300 MR. Carbon monoxide yield with the addition of nitrogen dioxide was greater than that with propane addition.

5. Conclusion

For the efficient utilization of heat from a high temperature reactor, the NIS process is a hopeful candidate of thermochemical processes for hydrogen production. The features of the process are,

- 1) Thermal efficiency of the process is estimated to be 30 - 40 %, assuming 70 - 80 % heat recovery.
- 2) Purity of hydrogen produced in reaction 1 is more than 97 %.
- 3) Large amount of heat is required at relatively low temperatures. The steps which absorb heat most are dehydration of mixed nickel salts and evaporation of ethanol from ethanol solution of nickel iodide.
- 4) In the highest temperature reaction, the reaction 3, neither water nor hydrogen takes parts.

Radiolysis of carbon dioxide is a suitable reaction for the radiation chemical hydrogen production process, and has the following features,

- 1) Only two reactions are required to close the cycle of water decomposition. Water decomposition results from the combination of the radiolysis reaction 10 and the water shift reaction 9.



- 2) Energy conversion efficiency in reaction 10 depends largely on the extent of reoxidation of carbon monoxide during the irradiation.
- 3) The reoxidation of carbon monoxide is suppressed by a small amount of additives, such as nitrogen dioxide, or propane.
- 4) Addition of nitrogen dioxide to carbon dioxide resulted in a higher carbon monoxide yield than that of propane.

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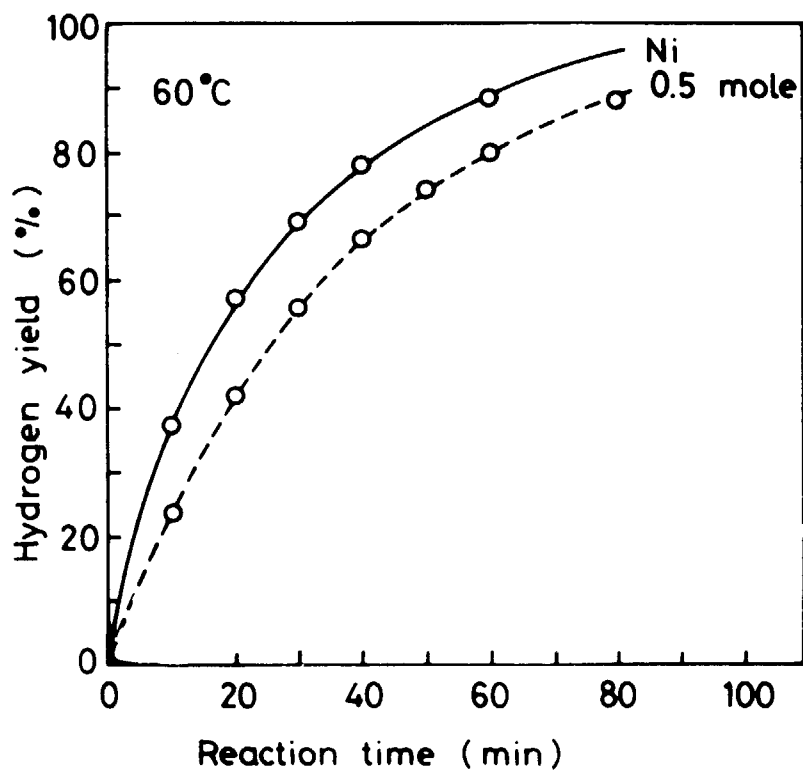


Fig. 1 Hydrogen evolution by reaction (1)
 HI(0.02 mol), H₂SO₄(0.01), Ni(0.5)
 ----- HI 27 w/o, H₂SO₄ 10 w/o
 ————— HI 35 w/o, H₂SO₄ 13 w/o

Table 1 Solubilities of NiI₂ and NiSO₄ in EtOH

Temperature (°C)	20	50
Solubility of NiI ₂ ^{a)}	58.3	135.4
Solubility of NiSO ₄ ^{b)}	0.018	0.024

Solubility: anhydrous nickel salt (g) in 100 g EtOH,
 a) observed, b) obtained by extrapolation from
 literature.^{4a)}

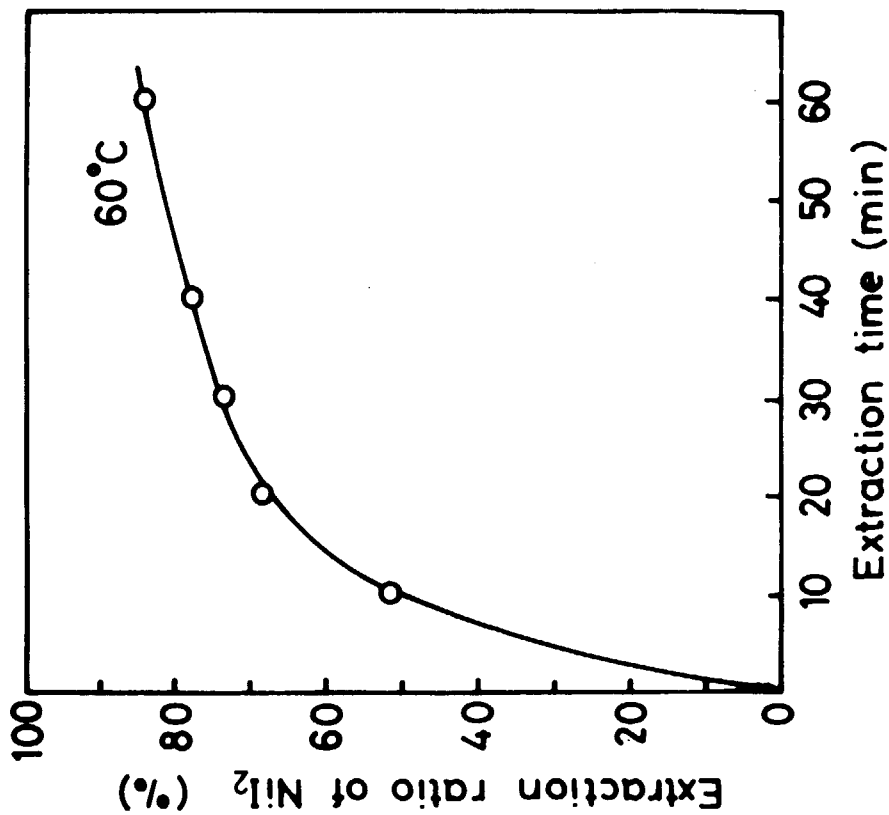


Fig. 2 Extraction of NiI₂ by EtOH

NiI₂ (0.04), NiSO₄ (0.04), EtOH(0.4 mole)

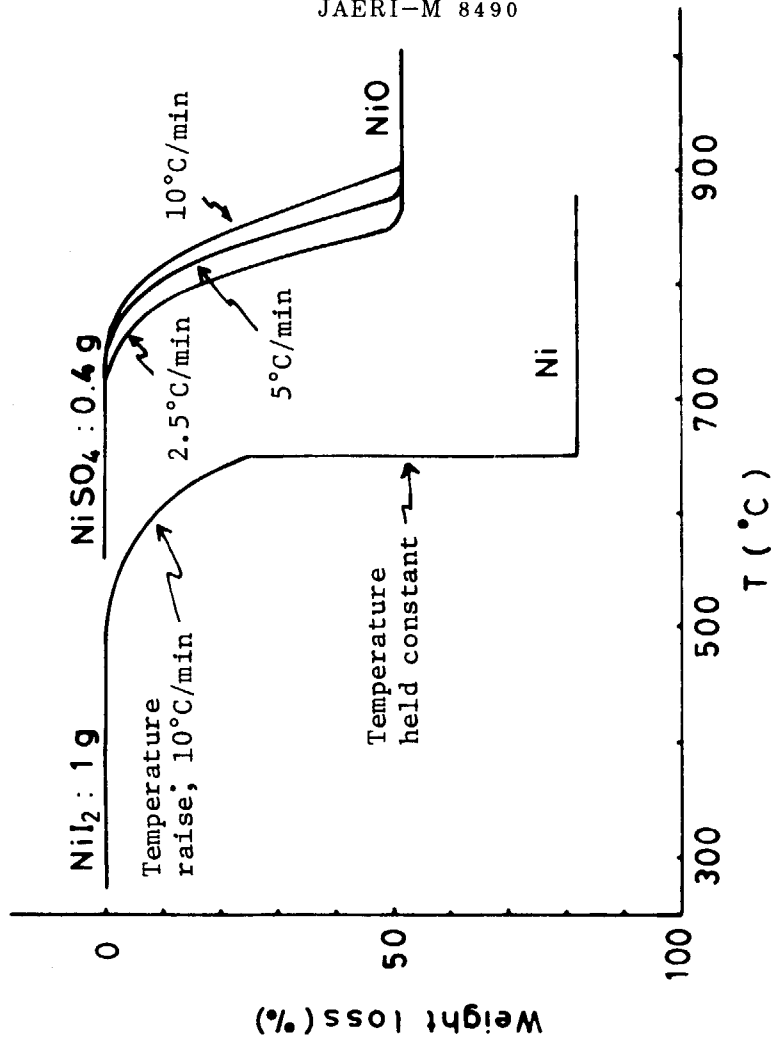


Fig. 3 Pyrolysis of NiI₂ and NiSO₄

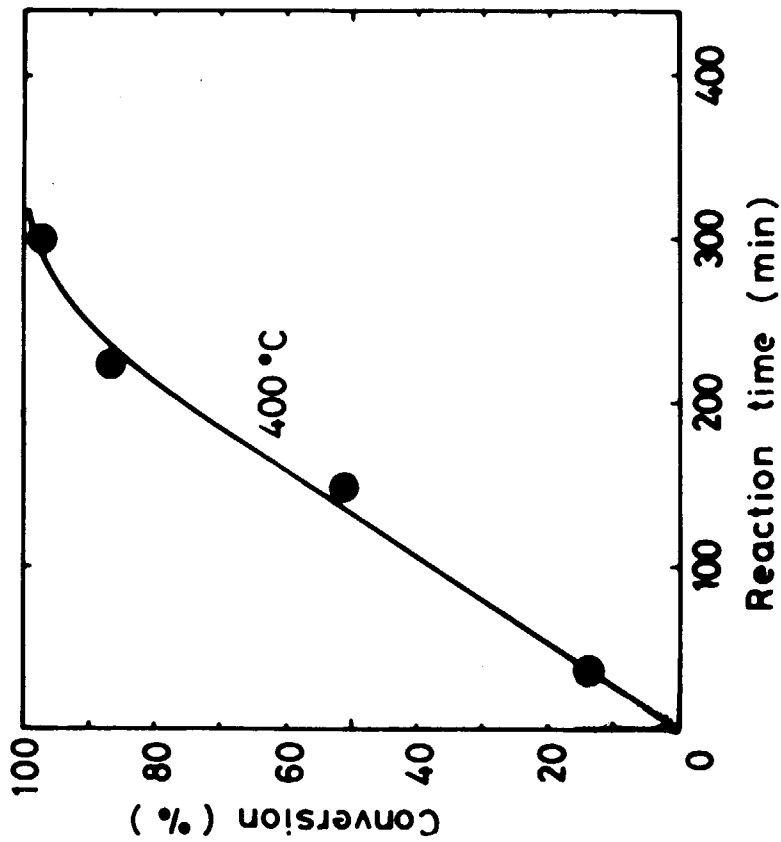


Fig. 4 Reduction of NiO

NiO: 3.5g, H₂ (30ml/min) in He (60ml/min)
400°C

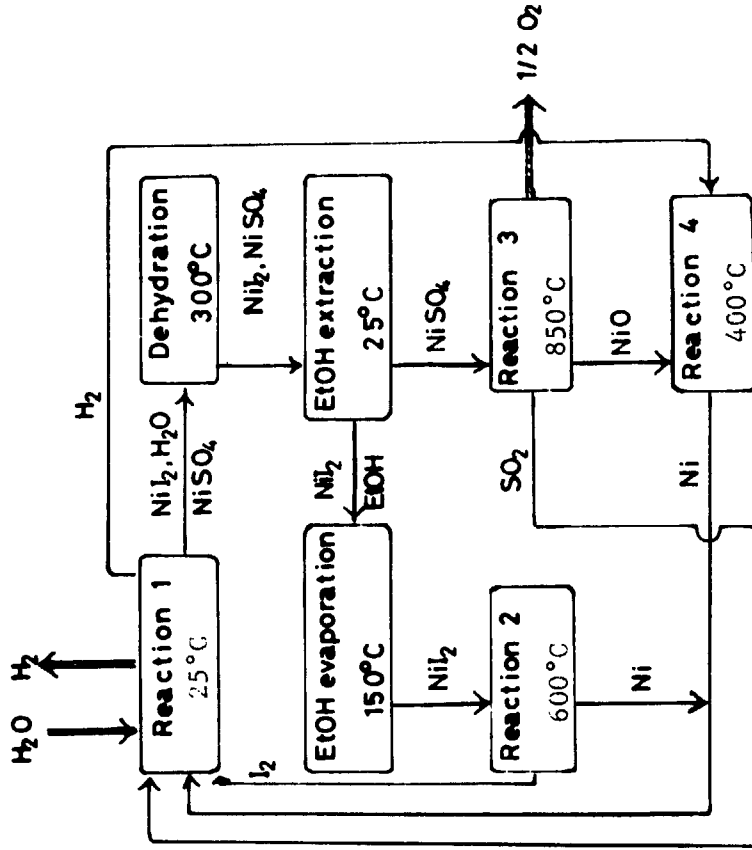


Fig. 5 Simplified flowsheet of NIS process

Table 2 Heat Balance of NIS Process

Step	Temp. (°C)	Q(kJ/molH ₂)
1. 2H ₂ O(l)+I ₂ (c)+SO ₂ (g)=2HI(aq)+H ₂ SO ₄ (aq)	25	-151.4
2. 2HI(aq)+H ₂ SO ₄ (aq)+2Ni(c)=NiI ₂ (aq)+NiSO ₄ (aq)+2H ₂ (g)	25	-107.8
3. NiI ₂ (aq)+NiSO ₄ (aq)=NiI ₂ (c)+NiSO ₄ (c)+20H ₂ O(g)	25→300	+1306.2
4. 20H ₂ O(g)=20H ₂ O(l)	300→25	-1065.2
5. NiI ₂ (c)+NiSO ₄ (c) cooling	300→25	-64.4
6. NiI ₂ (c)+10EtOH(l)=NiI ₂ (EtOH soln.)	25	-86.2
7. NiI ₂ (EtOH soln.)=NiI ₂ (c)+10EtOH(g)	25→150	+575.7
8. 10EtOH(g)=10EtOH(l)	150→25	-517.0
9. NiI ₂ (c) heating	150→600	+37.8
10. NiI ₂ (c)=Ni(c)+I ₂ (g)	600	+140.5
11. I ₂ (g)=I ₂ (c)	600→25	-87.9
12. Ni(c) cooling	600→25	-19.8
13. NiSO ₄ (c) heating	25→850	+131.1
14. NiSO ₄ (c)=NiO(c)+SO ₃ (g)	850	+238.1
15. SO ₃ (g)=SO ₂ (g)+1/2O ₂ (g)	850	+126.9
16. SO ₂ (g)+1/2O ₂ (g) cooling	850→25	-57.1
17. NiO(c) cooling	850→400	-28.9
18. H ₂ (g) heating	25→400	+11.0
19. NiO(c)+H ₂ (g)=Ni(c)+H ₂ O(g)	400	-5.4
20. H ₂ O(g)=H ₂ O(l)	400→25	-57.2
21. Ni(c) cooling	400→25	-12.9

Q₊=+2567.3Q₋=-2261.2Table 3 Reduction of Fe₃O₄ to FeX₂ by reaction with gaseous HX

HX	Fe ₃ O ₄ reacted (%)	FeX ₃ /FeX ₂
HCl	26.2	0.67
HBr	89.6	0.06
HI	98.6	0.00

Fe₃O₄; 10g, HX; 0.45 moles, 200 °C

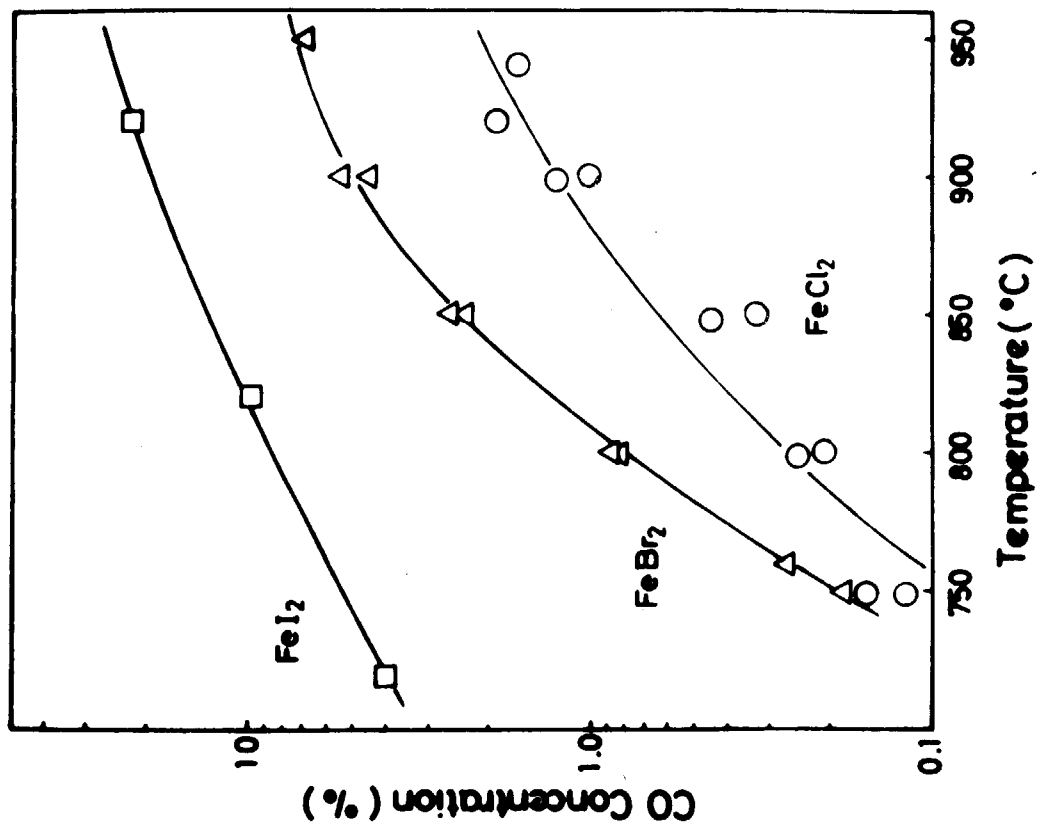


Fig. 6 CO formation from CO₂ - FeX₂ system.
 (Effect of reaction temperature)
 quartz reactor, FeX₂; 10g, CO₂; 30ml/min

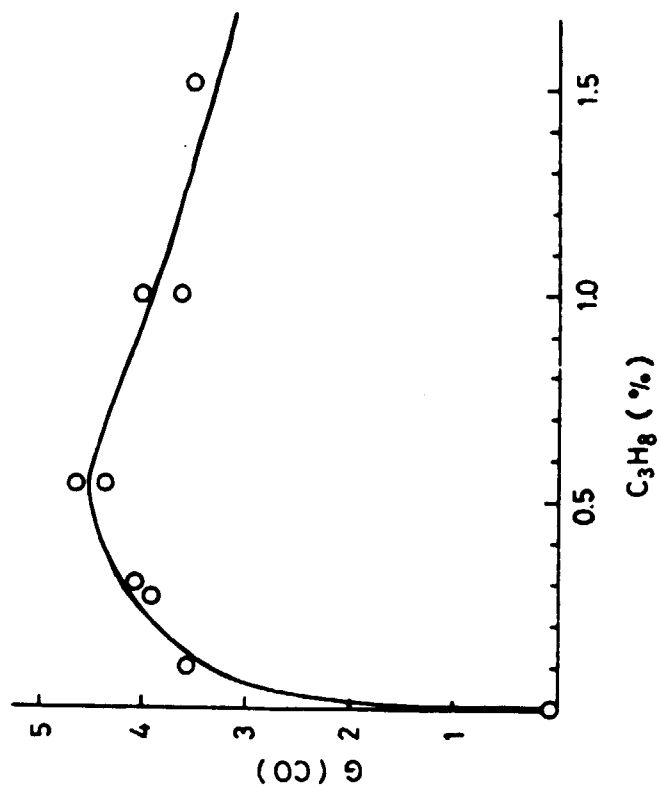


Fig. 7 Effect of propane addition
 160 ml glass ampoule, 1 atm,
 gamma-rays; 0.95 MR/h, 6.7 Mrad.

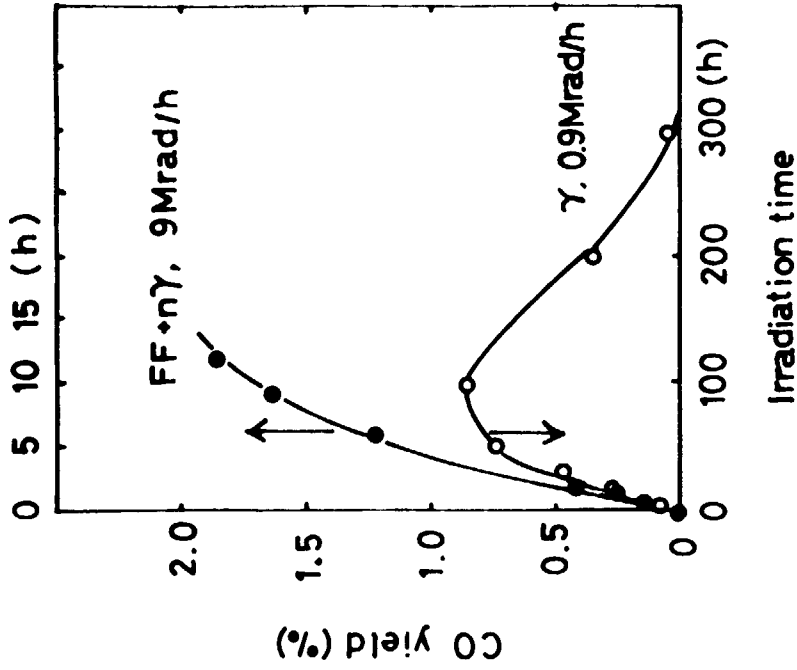


Fig. 9 CO formation by fission fragments and gamma-rays
99% CO₂+1% C₃H₈, 6 atm in 42 ml ampoule.

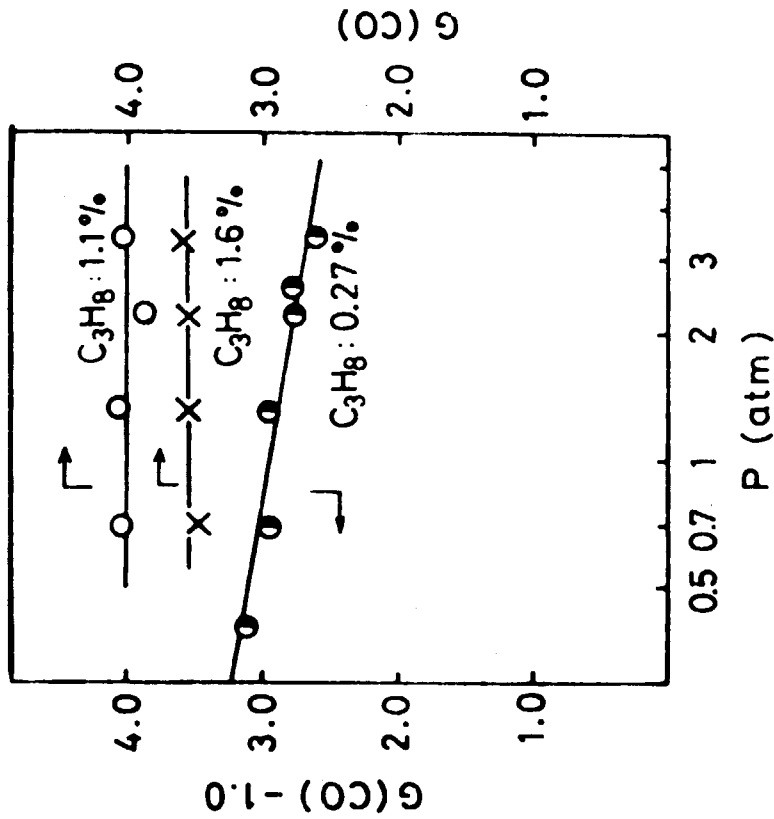


Fig. 8 Pressure dependence of G(CO)
64 and 160 ml glass ampoule,
gamma-rays; 0.95 MR/h, 6.7 Mrad.

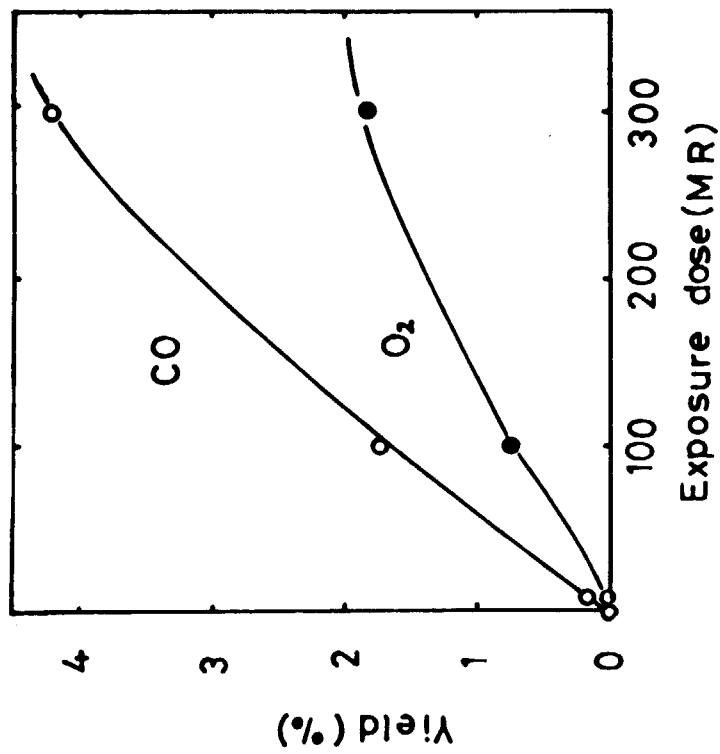


Fig. 10. Radiolysis of CO₂ by gamma-rays
99% CO₂+1% NO₂, 6 atm in 42 ml
ampoule.