DOE/JPL/956061-4
(DE82020508)

INVESTIGATION OF THE HYDROCHLORINATION OF $SiCl_4$

Flat-Plate Solar Array Project. Task I. Silicon Material

Quarterly Report for April 9—July 8, 1982

By
Jeffrey Y. P. Mui

July 12, 1982

Work Performed Under Contract No. NAS-7-100-956061

Solarelectronics, Inc.
Bellingham, Massachusetts

U.S. Department of Energy

Solar Energy

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DOE/JPL/956061-4
(DE82020508)
Distribution Category UC-63b

FLAT-PLATE SOLAR ARRAY PROJECT

TASK I SILICON MATERIAL

QUARTERLY REPORT

INVESTIGATION OF THE HYDROCHLORINATION OF $SiCl_4$

(Covering the Period April 9, 1982 to July 8, 1982)

JPL CONTRACT NO. 956061

TO

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

BY

JEFFREY Y. P. MUI

April 12, 1982.

The JPL Flat-Plate Solar Array Project is sponsored by the U. S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE.

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FLAT-PLATE SOLAR ARRAY PROJECT

SILICON MATERIAL TASK

"Investigation of the Hydrochlorination of $SiCl_4$"

FOURTH QUARTERLY REPORT

July 12, 1982.

by

Jeffrey Y. P. Mui

SOLARELECTRONICS, INC.

Bellingham, Mass.

ABSTRACT

The Program Plan was reviewed and revised in the fourth quarter. In place of "Fluidization Mechanism Study" (Item VIII), a more basic research oriented experimental study on the effect of pressure on the hydrochlorination of $SiCl_4$ was carried out. The revised Program Plan is shown in the Appendix.

Reaction kinetic measurements on the hydrochlorination of $SiCl_4$ and metallurgical grade (m.g.) silicon metal were made at a wide range of experimental variables. The effect of pressure on the reaction rate was studied at 25 psig, 100 psig, 150 psig and 200 psig, respectively. Results of this series of experiments show a large pressure effect on the hydrochlorination reaction. As expected, higher pressures produce a higher equilibrium $SiHCl_3$ conversion, since the hydrochlorination reaction results in a net volume contraction as product $SiHCl_3$ is formed.

$$3\ SiCl_4 + 2\ H_2 + Si = 4\ SiHCl_3 \qquad (1)$$

However, the reaction rate, namely, the rate at which the hydrochlorination reaction reaches its equilibrium $SiHCl_3$ conversion, was found to be much faster at low pressures.

Reaction kinetic measurements were also carried out at a low pressure of 100 psig as a function of temperatures and $H_2/SiCl_4$ feed ratios. One series of experiments was carried out at reaction temperature of 350°C, 400°C, 450°C and 500°C, respectively. As previously observed, a higher reaction temperature produces both a faster reaction rate and a higher equilibrium $SiHCl_3$ conversion. Another series of experiments was carried out at 500°C, 100 psig and with various $H_2/SiCl_4$ feed ratios of 1.0, 2.0, 2.8, 4.0 and 4.7, respectively. Results of this series of experiments show that a higher $H_2/SiCl_4$ feed ratio gives a higher conversion of $SiHCl_3$. A higher $H_2/SiCl_4$ feed ratio results a higher partial pressure of hydrogen gas in the hydrochlorination reactor. Thus, the higher partial pressure of hydrogen will drive the equilibrium reaction to the right hand side of equation (1) to produce more $SiHCl_3$. The variable $H_2/SiCl_4$ feed ratios do not appear to significantly effect the rate of the hydrochlorination reaction.

A corrosion test on various material of construction for the hydrochlorination reactor was last reported (see Third Quarterly Report, April 12, 1982). Analysis of the Alloy 400 test sample by a Scanning Electron Microscope (SEM) shows some interesting results. The SEM analysis on the Alloy 400 test sample provides further experimental evidences on the corrosion mechanism of metal alloys in the hydrochlorination reaction enviroment.

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I. INTRODUCTION

Experimental work on the hydrochlorination of $SiCl_4$ and m.g. silicon metal to produce $SiHCl_3$ was continued as scheduled in accordance with the revised Program Plan. This Quarterly Report is the fourth one in the series. The objective of this research and development program is to carry out an experimental study on the hydrochlorination reaction to generate basic reaction kinetic and engineering data so that the potential application of the hydrochlorination process for the production of high purity, solar grade silicon metal can be fully evaluated.

Activities in this quarter include reaction kinetic measurements on the hydrochlorination of $SiCl_4$ over a wide range of experimental variables and a corrosion mechanism study on metal alloys under the hydrochlorination reaction conditions. Results are summarized in the following discussion.

II. DISCUSSION

A. The Revised Program Plan

The Program Plan was reviewed and revised in the fourth quarter. The revised Program Plan is shown in the Appendix. More basic research oriented experimental studies are emphasized in future programs. In place of "Fluidization Mechanism Study" (Item VIII), a basic research and development program on the effect of pressure on the hydrochlorination reaction was carried out. Previously, experimental studies on the hydrochlorination of $SiCl_4$ and m.g. silicon metal were carried out at pressure range of 300 psig and 500 psig. To study the effect of pressure, experiments were carried out at the lower pressure range of 25 psig, 100 psig, 150 psig and 200 psig, respectively. The effect of temperature and $H_2/SiCl_4$ feed ratio on the hydrochlorination reaction was also studied at these low pressure ranges.

B. The Hydrochlorination Apparatus

The two inch-diameter stainless steel reactor for the hydrochlorination of $SiCl_4$ and m.g. silicon metal is schematically shown in Figure I. The design and operation of the hydrochlorination apparatus were reported in detail in the first Quarterly Report (DOE/JPL 956061-1). A low back pressure regulator and control assembly were installed for the planned hydrochlorination experiments at pressure range as low as 25 psig. The $H_2/SiCl_4$ feeding system was also modified to give a more accurate control on the $SiCl_4$ liquid temperature for these low pressure, high $H_2/SiCl_4$ feed ratio experiments. The hydrochlorination apparatus has been operated satisfactory. Results of the experimental work are summarized in the following.

C. Effect of Pressure on the Hydrochlorination Reaction

Since the hydrochlorination of $SiCl_4$ and m.g. silicon metal to form $SiHCl_3$ results in a net volume contraction,

$$3\ SiCl_4 + 2\ H_2 + Si = 4\ SiHCl_3$$

a higher reaction pressure shall produce a higher equilibrium conversion of $SiHCl_3$. Experimental results previously obtained on this reaction are in good agreement with the thermodynamics prediction. However, thermodynamic property of the hydrochlorination of $SiCl_4$ and m.g. silicon metal does not prescribe reaction kinetics. A small pressure effect on the reaction rate, i.e., the rate at which the hydrochlorination reaction reaches its equilibrium $SiHCl_3$ conversion, was noted in the previous experimental studies at 300 psig and at 500 psig(1). The reaction rate at 500 psig was slightly slower than that at 300 psig. A very noticable pressure effect on the reaction rate was observed in a preliminary experiment on the hydrochlorination reaction carried out at 73 psig (see Figure III Second Quarterly Report, January 9, 1982). In the revised Program Plan, the effect of pressure on the hydrochlorination of $SiCl_4$ and m.g. silicon metal is systematically studied over a wide range of experimental variables.

A series of experiments was carried out at 450°C, with a $H_2/SiCl_4$ feed ratio of 2.0 and at various pressures of 25 psig, 100 psig, 150 psig and 200 psig, respectively. Results of this series of experiments are summarized in Table I (25 psig), Table II (100 psig), Table III (150 psig) and Table IV (200 psig). Data in these four Tables are also presented in Figure II by plotting the % $SiHCl_3$ conversion versus residence time. As the thermodynamic property of the hydrochlorination reaction predicts, results in Figure II show that a higher reaction pressure produces a higher conversion of $SiHCl_3$ close to equilibrium at long residence times. On the other hand, the reaction rates are noticably slower at higher pressures. For example at 25 psig, the kinetic curve in Figure II starts leveling off (approaches equilibrium) at about 60 seconds residence time. At pressures over 100 psig, the hydrochlorination reaction has not yet reached equilibrium with the residence time as shown in Figure II.

Another series of experiments on the hydrochlorination of $SiCl_4$ and m.g. silicon metal was carried out at 500°C with the same $H_2/SiCl_4$ feed ratio of 2.0 and the same pressure range of 25 psig, 100 psig, 150 psig and 200 psig, respectively. Results of these experiments are summarized in Table V, Table VI, Table VII and Table VIII, respectively. Data in these four Tables are also presented in Figure III by plotting the % $SiHCl_3$ conversion versus residence time. The profiles of the kinetic curves in Figure III are similar to those in Figure II to show the same pressure effect on the hydrochlorination reaction. The generally higher $SiHCl_3$ conversion at 500°C in Figure III is the combined results of the pressure effect and of the temperature effect. As previous experimental studies on the hydrochlorination reaction show, a higher reaction temperature produces both a faster reaction rate and a higher equilibrium conversion of $SiHCl_3$. For example, the reaction at 25 psig resulted an equilibrium conversion of about 18% $SiHCl_3$ at 500°C (Figure III).

At 450°C, an equilibrium conversion of about 16% $SiHCl_3$ is obtained at the same pressure of 25 psig (Figure II). Also, the rate of approaching equilibrium at 500°C is faster than that at 450°C. For example, the reaction takes about 15 seconds residence time to reach 90% of its equilibrium $SiHCl_3$ conversion (0.9 x 18% = 16.2%) at 500°C. At 450°C, the same reaction requires about 26 seconds residence time to reach the same 90% equilibrium conversion of $SiHCl_3$ (0.9 x 16% = 14.4%). The effect of temperature on the hydrochlorination reaction is further studies in the following experiments.

D. <u>Effect of Temperature on the Hydrochlorination Reaction</u>

A series of experiments was carried out to study the effect of temperature on the hydrochlorination reaction at 100 psig, with a $H_2/SiCl_4$ feed ratio of 2.0 and at reaction temperature of 350°C and 400°C to supplement the reaction kinetic data obtained at 450°C (Table II) and 500°C (Table VI). Results of these two experiments are summarized in Table IX and Table X for the reaction kinetic data obtained at 350°C and 400°C, respectively. The experimental results obtained at these four reaction temperatures are presented in Figure IV by plotting the % $SiHCl_3$ conversion versus residence time. Data in Figure IV show that a large temperature effect on the hydrochlorination reaction is evident. The kinetic curves at 500°C and 450°C level off at the equilibrium conversion of $SiHCl_3$ while the kinetic curves at 400°C and 350°C are far from reaching equilibrium with the residence time as shown in Figure IV. As previously observed, a higher reaction temperature gives both a faster reaction rate and a higher equilibrium conversion of $SiHCl_3$. For example at 500°C, the hydrochlorination reaction reaches 90% of its equilibrium $SiHCl_3$ conversion in about 35 seconds residence time. At 450°C, about 68 seconds residence time is needed for the hydrochlorination reaction to achieve the same 90% equilibrium $SiHCl_3$ conversion. At 500°C, the equilibrium $SiHCl_3$ conversion is about 2% to 3% higher than that of the equilibrium $SiHCl_3$ conversion at 450°C.

E. Effect of $H_2/SiCl_4$ Feed Ratio on the Hydrochlorination Reaction

The effect of $H_2/SiCl_4$ feed ratio on the hydrochlorination reaction was studied at 100 psig and at 500°C. The reaction temperature and pressure were kept constant at 500°C and 100 psig while the $H_2/SiCl_4$ feed ratio was varied at 1.0, 2.0, 2.8, 4.0 and 4.7, respectively. Results of these experiments are summarized in Table XI (1.0), Table VI (2.0), Table XII (2.8), Table XIII (4.0) and Table XIV (4.7). Data in these Tables are also presented in Figure V by plotting the % $SiHCl_3$ conversion versus residence time. As results in Figure V show, a higher $H_2/SiCl_4$ feed ratio produces a higher conversion of $SiHCl_3$. This is expected from an equilibrium reaction,

$$3\ SiCl_4 + 2\ H_2 + Si = 4\ SiHCl_3$$

An increase of the $H_2/SiCl_4$ feed ratio corresponds to an increase of the hydrogen partial pressure in the hydrochlorination reactor. A higher partial pressure of hydrogen gas drives the equilibrium toward the right hand side of the equation to produce more $SiHCl_3$. The varying $H_2/SiCl_4$ feed ratios do not appear to significantly effect the reaction rate, since the profiles of the kinetic curves in Figure V are very similar to one another.

F. Hydrochlorination of $SiCl_4$ and M.G. Silicon Metal at Low Pressures

Previous experimental studies on the hydrochlorination of $SiCl_4$ and m.g. silicon metal were carried out at pressure range of 300 psig and 500 psig. The upper 500 psig pressure range was the operating pressure selected by Union Carbide Corporation in their design on the 100 metric tons per year Experimental Process System Development Unit (EPSDU) under JPL Contract No. 954334[2]. The higher pressure range of 500 psig has the advantage of a greater mass through put and a higher, achievable equilibrium conversion of $SiHCl_3$. This, presumably, is the basis for operating the hydrochlorination process at the highest, practical pressure range. However, the present experimental study on the hydrochlorination reaction at the lower pressure range of 25 psig to 200 psig shows that it can be advantageous to carry out the hydrochlorination process at low pressures. The reaction rate was found to be faster at lower pressures. Thus, the faster reaction rate partially conpensates for the lower mass through put in operating the hydrochlorination reactor at a lower pressure. If it is needed, one can raise the reaction temperature to increase the reaction rate still further and the equilibrium conversion of $SiHCl_3$. For example, depending on the material of construction, a hydrochlorination reactor designed for 500 psig, 500°C may be operated at a lower pressure of 100 psig, but at a higher temperature of 550° - 600° C. The combined effects of a lower pressure and a higher temperature on the reaction rate can increase the output of product $SiHCl_3$ to the same level as those at the higher pressure range. In order words, it can be advantageous to operate the hydrochlorination process at low pressures without sacrificing the output of product $SiHCl_3$ from a given reactor size. In certain cases, one may need to operate the hydrochlorination process at low pressures. For example, if one incorporates the hydrochlorination reaction into a Siemens type process to form a closed-loop operation for the production of high purity silicon metal, it may not be desirable to back-integrate a high pressure unit operation to a low pressure manufacturing process. The objective of the present experimental study on the hydrochlorination of $SiCl_4$ and m.g. silicon metal is to expand the scope of these basic reaction kinetic measurements to cover the reaction conditions at low pressures.

G. Corrosion Mechanism Study

A corrosion test was conducted during the last quarter to evaluate a variety of metals and alloys as material of construction for the hydrochlorination reactor under the actual reaction conditions. Results of the corrosion study show that a silicide protective film was formed on the metal alloy surface. The silicide protective film on the nickel and on the Incoloy 800H test samples was analyzed by a Scanning Electron Microscope (see third Quarterly Report, April 12, 1982). Results of the Scanning Electron Microscopic (SEM) analysis on the Alloy 400 test sample were completed this quarter. Alloy 400 (2/3 Ni, 1/3 Cu) is an interesting case. The amount of silicon deposition on Alloy 400 (4 m.g./cm^2) is less than those of the pure elements, nickel (15 m.g./cm^2) and copper (15 m.g./cm^2). With pure nickel and pure copper, the nickel silicide film and the copper silicide film are formed by the simple combination of two elements. With Alloy 400, formation of the silicide film is more complex, since other copper-nickel phases in the base alloy are involved in the process. The smaller silicon deposition on Alloy 400 may be explained as a higher activation energy process, since the copper-silicon and the nickel-silicon phases in the silicide protective film are now produced at the expenses of the copper-nickel phases which make up the base alloy. Results of the SEM analysis on the Alloy 400 test sample provide further experimental evidence on the mechanism of the formation of the silicide protective film on the metal alloy surface under the hydrochlorination reaction conditions.

Figure VI shows the SEM photographs of the surface of the silicide protective film on the Alloy 400 test sample. The surface morphology has a rather porous structure. This porous structure is also seen in the SEM photograph of a cross sectional area of the silicide film as show in Figure VII. The cross section of the silicide film shows many void spaces. The X-ray distribution maps of nickel, copper and silicon in Figure VII show some interesting results. The copper X-ray distribution map shows a copper-rich zone at the surface of the silicide film and at the surface of the base alloy. On the other hand, the nickel X-ray distribution map shows that nickel is depleted at the surface of the base alloy where the copper concentration is enriched. The mechanism on the formation of the silicide protective film on the metal alloy surface was postulated (see third Quarterly Report) as a chemical vapor deposition of silicon from the hydrochlorination reaction followed by the thermal diffusion of silicon and the metallic elements to and from the base alloy to form stable metal-silicon phases which make up the bulk of the silicide protective film. The high concentration of copper near the surface of the silicide film on Alloy 400 (Monel) may be explained by the formation of the thermodynamically more stable (lower melting) copper-silicon phases, e.g., Cu_3Si m.p. 558°, 802°C. As silicon is deposited onto the alloy surface, it preferentially alloys with copper to form a copper-rich zone. As the silicide film grows, silicon from the surface must diffuse into the alloy body. At the same time, nickel and copper can thermally diffuse and interact with silicon to form stable nickel-silicon and copper-silicon phases which make up the silicide film. Results of the SEM analysis show that the homogeneous copper-nickel alloy base is segregated into copper-rich and nickel-rich zones in the silicide film (Figure VII). As the silicide film continues to grow, the copper-nickel phases in the base alloy must be broken up and interact with silicon to form the variety of copper-silicon and nickel-silicon phases. This mechanism on the formation of the silicide film is in agreement with the SEM results. The slower grow (less silicon deposition) of the silicide film on Alloy 400 in comparison with pure nickel and pure copper can be explained by a slower kinetic process, since the copper-silicon and the nickel-silicon phases in the silicide film are now formed at the expense of the nickel-copper phases in the base alloy.

The segregation of copper and nickel in the silicide protective film is also show by the X-ray microprobe and the EDAX analyses of four different areas at the cross section of the silicide film. Results of these analyses are shown in Figure VIII. The atomic composition of Area #1 near the surface of the silicide film confirms the high concentration of copper (52.22%). The nickel concentration in Area #1 (11.22%) is low in comparison with those in Area #2 (48.42%) and Area #3 (55.31%) at the middle section of the silicide film. In the middle section, the copper concentrations are low (Area #2, 9.24% and Area #3, 3.99%) in comparison with that of Area #1. On the other hand, the silicon concentration is relatively constant in these three areas: Area #1, 36.55%; Area #2, 40.88% and Area #3, 38.77%. The base alloy (Area #4) has the composition of about 61% nickel and 35% copper in agreement with the specification of Alloy 400 (Monel).

H. Summary of Progress

Experimental work on the JPL Contract No. 956061 has progressed on schedule in accordance with the revised Program Plan. The effect of pressure on the hydrochlorination of $SiCl_4$ and m.g. silicon metal was systematically studied. A significant pressure effect on the hydrochlorination reaction was measured over a wide range of reaction conditions. These low pressure experiments provide basic reaction kinetic data to supplement the previously obtained reaction kinetic data at the high pressure range. SEM analysis on the Alloy 400 test sample has provided further experimental evidence on the mechanism of corrosion of metals and alloys in the hydrochlorination reaction enviroment.

III. FUTURE ACTIVITIES

The one-year research and development program (JPL Contract No. 956061) expires on July 30, 1982. All the planned experimental studies as shown in the Program Plan have been completed. An extension of this contractual work has been proposed to Jet Propulsion Laboratory to carry out further fundamental studies on the hydrochlorination of $SiCl_4$ and m.g. silicon metal. This proposal is in the process of being evaluated by Jet Propulsion Laboratory.

IV. REFERENCES

(1) Final Report, JPL Contract No. 955382, "Investigation of the Hydrogenation of $SiCl_4$" by Jeffrey Y. P. Mui and Dietmar Seyferth, Massachusetts Institute of Technology, April 15, 1981.

(2) Final Report, JPL Contract No. 954334, "Feasibility of the Silane Process for Producing Semiconductor Grade Silicon", Union Carbide Corporation, June, 1979.

V. APPENDIX

Program Plan

Table I to XIV

Figure I to VIII

SC-1 PROGRAM PLAN JPL/SOLARELECTRONICS CONTRACT NO. 956 061

Year	1981						1982					
Month of Year	7	8	9	10	11	12	1	2	3	4	5	6
Month of Contract	1	2	3	4	5	6	7	8	9	10	11	12
I Program Plan, Baseline Cost Est.	~~1~~											
II Transfer Reactor form M.I.T.	~~1~~	~~2~~										
III Reactor Design, Order Equipment Construction of Apparatus	~~1~~	~~2~~	~~3~~	~~4~~								
IV Safety Review, Start-up Reactor				~~4~~								
V Reaction Kinetics Measurement							▲					
(1) Function of T, P, C				~~4~~	~~5~~	~~6~~	~~7~~					
(2) Impurities Measurement					~~5~~	~~6~~	~~7~~					
(3) Mass Balance						~~6~~	~~7~~					
VI Corrosion Study									▲			
(1) Type 304,316 S.St., Incoloy, Alloy Steel, Carbon Steel etc.						~~6~~	~~7~~	~~8~~	~~9~~			
(2) Corrosion Mechanism Study								~~8~~	~~9~~	~~10~~		
VII By-Product HCl Recycle									▲			
(1) Reaction Kinetics with HCl						~~6~~	~~7~~	~~8~~	~~9~~			
(2) Data Evaluation							~~7~~	~~8~~	~~9~~			
VIII Effect of Reactor Pressure												▲
(1) Reaction Kinetic Measurements at Low Pressures										~~10~~	~~11~~	~~12~~
(2) Atmospheric to 500 psig.										~~10~~	~~11~~	~~12~~
(3) Temperature 350° - 500° C.												
(4) $H_2/SiCl_4$ Feed Ratio 1.0 - 5.0										~~10~~	~~11~~	~~12~~
(5) Data Evaluation										~~10~~	~~11~~	~~12~~
IX Recommendations									▲			▲
(1) Optimum Process Parameters									~~9~~			~~12~~
(2) Optimum Material for Reactor									~~9~~			
(3) Additional Development Work												~~12~~
(4) Final Report												12

▲ Milestone Check Points

Prepared by: Jeffrey Y. P. Mui , Solarelectronics, Inc.
July 22,1981. Revised April 26, 1982.

TABLE I

THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON METAL AT 25 PSIG, 450°C AND $H_2/SiCl_4$ FEED RATIO OF 2.0

Sample No.	Hydrogen Feedrate SLM (1)	Residence Time Second	Product Composition, Mole % SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	0.37	81.9	0.09927	15.98	83.92
2	0.37	81.9	0.08745	16.13	83.78
3	0.55	55.1	0.1071	15.37	84.52
4	0.55	55.1	0.1458	15.52	84.33
5	0.88	34.4	0.09545	14.72	85.18
6	0.88	34.4	0.1098	14.96	84.93
7	1.17	25.9	0.07396	14.32	85.61
8	1.17	25.9	0.08641	14.31	85.60
9	1.48	20.5	<0.05	13.70	86.30
10	1.48	20.5	<0.05	13.77	86.23
11	1.89	16.0	<0.05	12.98	87.02
12	1.89	16.0	<0.05	13.11	86.89

(1) SLM, Standard Liter per Minute

TABLE II

THE HYDROCHLORINATION OF $SiCl_3$ AND M.G. SILICON METAL AT 100 PSIG, 450° C AND $H_2/SiCl_4$ FEED RATIO OF 2.0

Sample No.	Hydrogen Feedrate SLM	Residence Time Second	Product Composition, Mole % SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	0.5	179	0.3040	19.74	79.95
2	0.5	179	0.3119	20.13	79.56
3	1.1	81.4	0.2515	18.24	81.51
4	1.1	81.4	0.2525	18.60	81.15
5	2.1	42.6	0.1764	15.47	84.35
6	2.1	42.6	0.2408	15.42	84.33
7	4.2	21.3	< 0.05	12.47	87.52
8	4.2	21.3	< 0.05	11.72	88.28

TABLE III

THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON METAL AT 150 PSIG, 450°C AND $H_2/SiCl_4$ FEED RATIO OF 2.0

Sample No.	Hydrogen Feedrate SLM	Residence Time Second	Product Composition, Mole % SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	0.67	183	0.6027	23.64	75.73
2	0.67	183	0.5873	23.90	75.51
3	1.02	120	0.4889	22.04	77.47
4	1.02	120	0.4401	22.09	77.47
5	1.57	78.1	0.3653	19.45	80.15
6	1.57	78.1	0.2910	18.94	80.77
7	2.35	52.2	0.2729	16.91	82.81
8	2.35	52.2	0.1756	17.17	82.66
9	3.8	32.3	0.1191	13.47	86.41
10	3.8	32.3	0.09731	13.21	86.69

TABLE IV

THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON METAL AT 200 PSIG, 450°C AND $H_2/SiCl_4$ FEED RATIO OF 2.0

Sample No.	Hydrogen Feedrate SLM	Residence Time Second	Product Composition, Mole % SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	0.86	198	0.6480	25.94	73.41
2	0.86	198	0.7101	26.05	73.24
3	1.25	136	0.4718	24.61	74.92
4	1.25	136	0.4971	24.16	75.34
5	1.96	86.9	0.3052	20.03	79.66
6	1.96	86.9	0.2842	20.29	79.43
7	2.65	64.3	0.2192	17.98	81.80
8	2.65	64.3	0.2380	17.61	82.16
9	4.05	42.0	0.1724	14.82	85.01
10	4.05	42.0	0.08395	15.07	84.85

TABLE V

THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON METAL
AT 25 PSIG, 500° C AND $H_2/SiCl_4$ FEED RATIO OF 2.0

Sample No.	Hydrogen Feedrate SLM (1)	Residence Time Second	Product Composition, Mole % SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	0.38	73.8	0.1684	18.16	81.67
2	0.38	73.8	0.1483	18.13	81.73
3	0.55	51.0	0.1354	17.89	81.97
4	0.55	51.0	0.1373	17.88	81.98
5	0.82	34.2	0.1841	17.43	82.39
6	0.82	34.2	0.1389	17.63	82.23
7	1.48	18.9	0.1639	16.96	82.87
8	1.48	18.9	0.1312	17.05	82.82
9	2.10	13.4	0.1022	16.41	83.49
10	2.10	13.4	0.1091	16.40	83.49

(1) SLM, Standard Liter per Minute

TABLE VI

THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON METAL AT 100 PSIG, 500°C AND $H_2/SiCl_4$ FEED RATIO OF 2.0

Sample No.	Hydrogen Feedrate SLM	Residence Time Second	Product Composition, Mole % SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	0.6	137	0.4614	22.90	76.64
2	0.6	137	0.4954	22.77	76.74
3	1.2	68.5	0.4091	21.97	77.62
4	1.2	68.5	0.3854	22.08	77.54
5	2.4	34.3	0.3316	20.53	79.13
6	2.4	34.3	0.3203	20.46	79.22
7	4.8	17.1	0.2423	18.20	81.56
8	4.8	17.1	0.2068	17.62	82.17

TABLE VII

THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON METAL AT 150 PSIG, 500°C AND $H_2/SiCl_4$ FEED RATIO OF 2.0

Sample No.	Hydrogen Feedrate SLM	Residence Time Second	Product Composition, Mole % SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	0.65	173	0.7586	27.47	71.77
2	0.65	173	0.7333	27.65	71.62
3	0.98	115	0.7298	26.85	72.42
4	0.98	115	0.7043	26.39	72.90
5	1.43	78.6	0.5694	24.37	75.06
6	1.43	78.6	0.4978	24.39	75.11
7	2.1	53.5	0.3594	22.48	77.16
8	2.1	53.5	0.4680	22.72	76.81
9	3.3	34.1	0.3718	19.14	80.49
10	3.3	34.1	0.3366	19.02	80.64

TABLE VIII

THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON METAL AT 200 PSIG, 500°C AND $H_2/SiCl_4$ FEED RATIO OF 2.0

Sample No.	Hydrogen Feedrate SLM	Residence Time Second	Product Composition, Mole % SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	0.82	190	0.7714	30.77	68.46
2	0.82	190	0.8315	30.67	68.50
3	1.24	126	0.8581	29.85	69.30
4	1.24	126	0.8830	30.05	69.06
5	1.82	85.6	0.6148	26.99	72.39
6	1.82	85.6	0.5398	27.35	72.11
7	2.50	62.3	0.4637	23.99	75.54
8	2.50	62.3	0.4790	24.18	75.34
9	3.75	41.5	0.3171	21.66	78.03
10	3.75	41.5	0.4346	21.56	78.00

TABLE IX

THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON METAL AT 100 PSIG, 350°C AND $H_2/SiCl_4$ FEED RATIO OF 2.0

Sample No.	Hydrogen Feedrate SLM (1)	Residence Time Second	Product Composition, Mole % SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	0.6	167	< 0.05	6.038	93.96
2	0.6	167	< 0.05	6.232	93.77
3	1.5	66.8	< 0.05	2.723	97.28
4	1.5	66.8	< 0.05	2.876	97.12
5	2.8	35.8	< 0.05	1.836	98.16
6	2.8	35.8	< 0.05	1.964	98.04
7	4.0	25.1	< 0.05	1.254	98.75
8	4.0	25.1	< 0.05	1.411	98.59

(1) SLM, Standard Liter per Minute

TABLE X

THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON METAL AT 100 PSIG, 400°C AND $H_2/SiCl_4$ FEED RATIO OF 2.0

Sample No.	Hydrogen Feedrate SLM	Residence Time Second	Product Composition, Mole %		
			SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	0.6	161	0.07554	13.18	86.74
2	0.6	161	0.08251	13.55	86.36
3	1.2	80.5	< 0.05	8.986	91.01
4	1.2	80.5	< 0.05	9.183	90.82
5	1.9	50.8	< 0.05	7.494	92.51
6	1.9	50.8	< 0.05	7.646	92.35
7	3.3	29.2	< 0.05	5.608	94.39
8	3.3	29.2	< 0.05	5.656	94.34

TABLE XI

THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON METAL AT 100 PSIG, 500°C AND $H_2/SiCl_4$ FEED RATIO OF 1.0

Sample No.	Hydrogen Feedrate SLM (1)	Residence Time Second	Product Composition, Mole % SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	0.4	154	0.3730	18.98	80.65
2	0.4	154	0.3464	18.71	80.94
3	0.7	88.0	0.2847	18.34	81.38
4	0.7	88.0	0.3317	18.29	81.38
5	1.1	56.0	0.2877	17.77	81.95
6	1.1	56.0	0.2420	17.62	82.14
7	2.0	30.8	0.2161	16.44	83.34
8	2.0	30.8	0.2103	16.25	83.54
9	3.5	17.6	0.1775	15.07	84.75
10	3.5	17.6	0.1729	14.33	85.50

(1) SLM, Standard Liter per Minute

TABLE XII

THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON METAL AT 100 PSIG, 500°C AND $H_2/SiCl_4$ FEED RATIO OF 2.8

Sample No.	Hydrogen Feedrate SLM	Residence Time Second	Product Composition, Mole %		
			SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	0.6	154	0.5759	24.49	74.94
2	0.6	154	0.5298	24.46	75.01
3	1.2	77.0	0.4124	23.64	75.95
4	1.2	77.0	0.5521	23.84	75.61
5	2.1	44.0	0.3953	23.09	76.51
6	2.1	44.0	0.5299	22.73	76.74
7	4.15	22.3	0.4223	21.29	78.29
8	4.15	22.3	0.4329	20.69	78.88

TABLE XIII

THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON METAL AT 100 PSIG, 500°C AND $H_2/SiCl_4$ FEED RATIO OF 4.0

Sample No.	Hydrogen Feedrate SLM	Residence Time Second	Product Composition, Mole % SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	0.7	145	0.6050	26.54	72.86
2	0.7	145	0.5453	26.85	72.61
3	1.2	84.6	0.5820	26.50	72.92
4	1.2	84.6	0.5479	26.72	72.73
5	2.1	48.3	0.4983	25.66	73.84
6	2.1	48.3	0.4669	25.23	74.30
7	4.2	24.2	0.4479	22.11	77.44
8	4.2	24.2	0.4267	21.81	77.76

TABLE XIV

THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON METAL AT 100 PSIG, 500°C AND $H_2/SiCl_4$ FEED RATIO OF 4.7

Sample No.	Hydrogen Feedrate SLM	Residence Time Second	Product Composition, Mole % SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	0.65	163	0.6244	28.12	71.26
2	0.65	163	0.7960	27.85	71.35
3	0.9	118	0.6961	27.47	71.83
4	0.9	118	0.6743	27.70	71.62
5	1.2	88.3	0.6617	26.61	72.73
6	1.2	88.3	0.6504	27.18	72.17
7	2.4	44.1	0.6020	25.84	73.56
8	2.4	44.1	0.5812	26.06	73.36
9	4.1	25.8	0.2576	24.64	75.10
10	4.1	25.8	0.2655	24.51	75.23

FIGURE I APPARATUS FOR THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON METAL TO $SiHCl_3$

(DRAWING NOT TO SCALE)

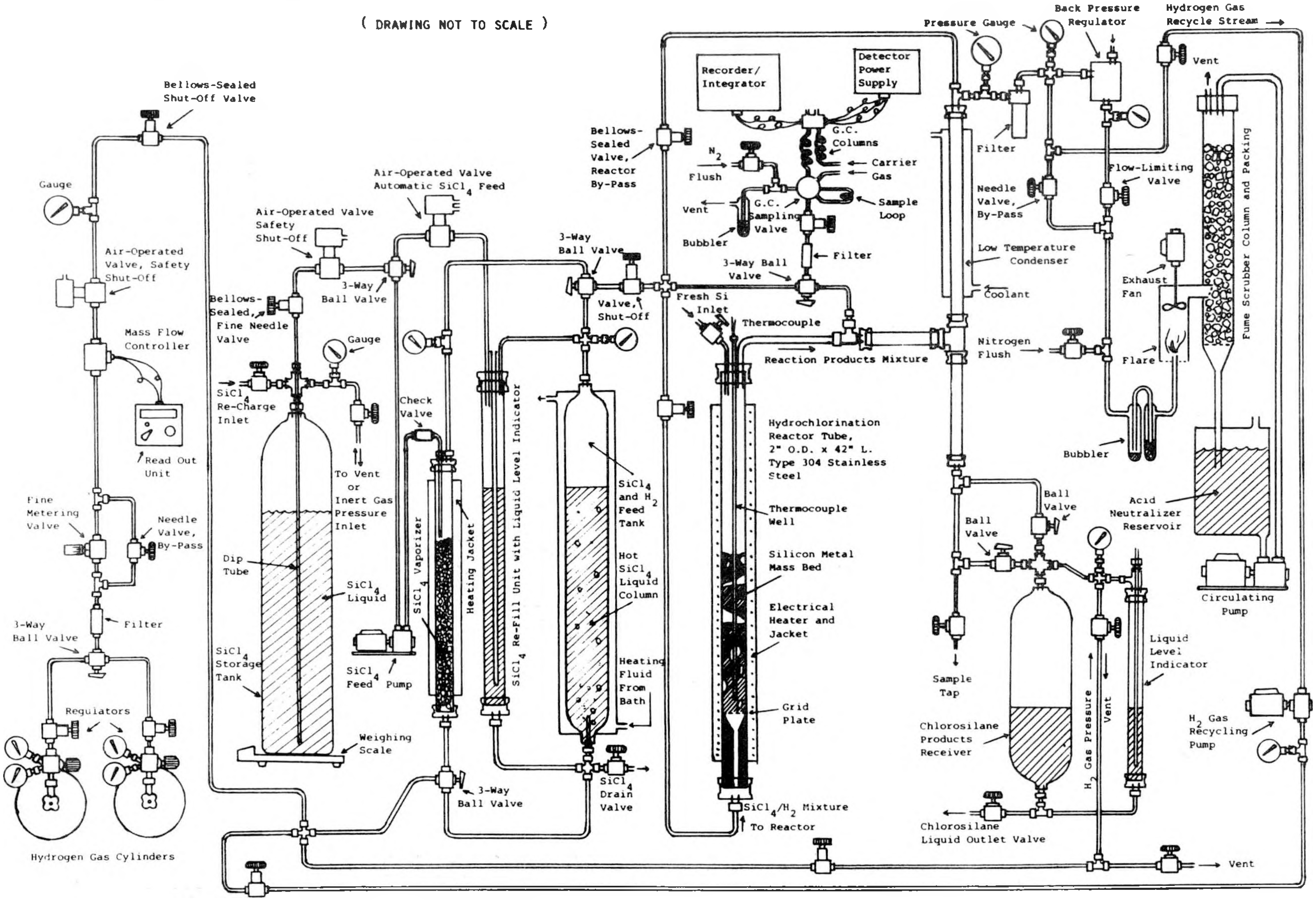


FIGURE II HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 450°C, $H_2/SiCl_4$ RATIO OF 2.0 AND AT VARIOUS PRESSURES

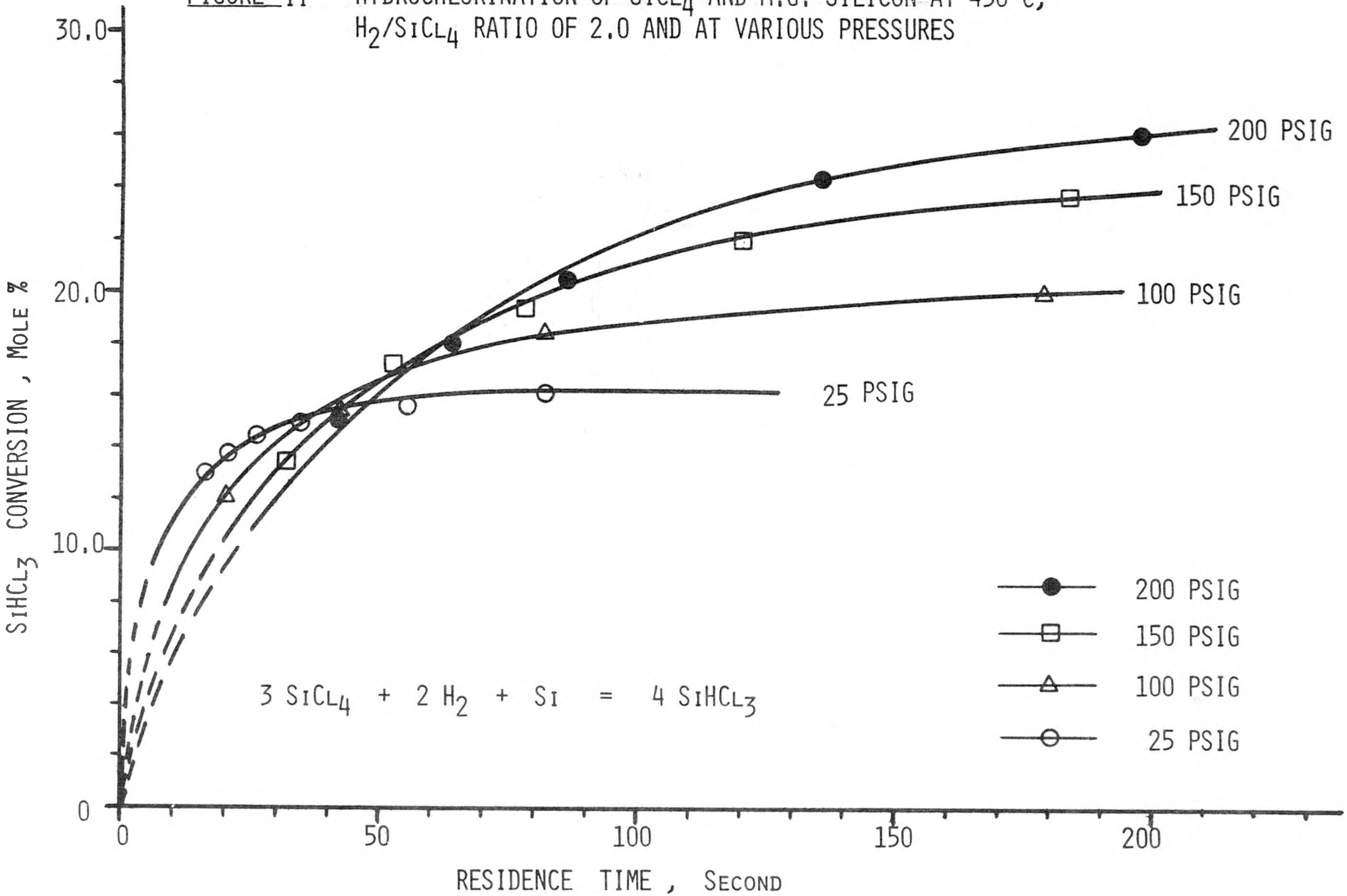


FIGURE III HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 500°C, $H_2/SiCl_4$ RATIO OF 2.0 AND AT VARIOUS PRESSURES

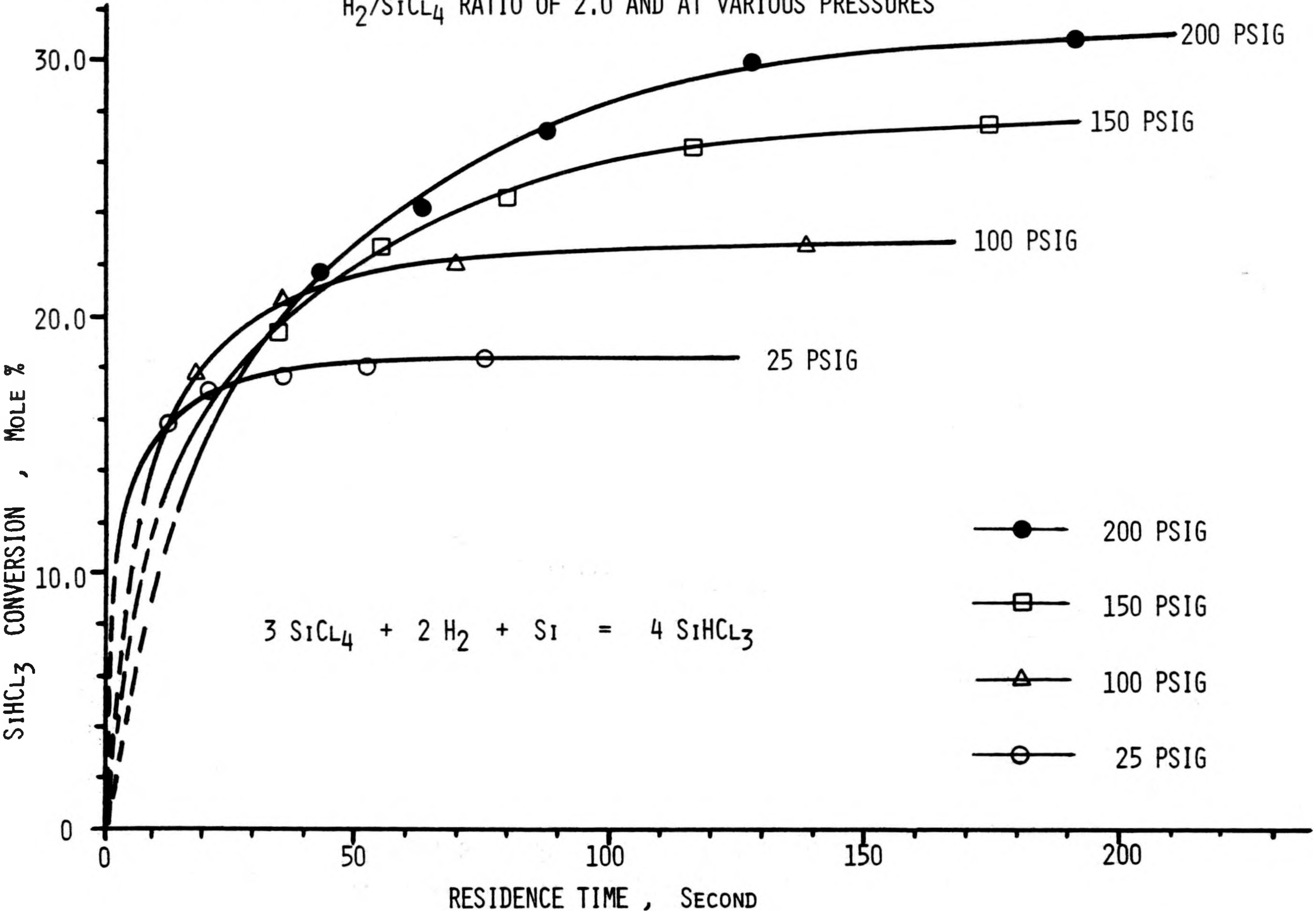


FIGURE IV THE EFFECT OF TEMPERATURE ON THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 100 PSIG AND $H_2/SiCl_4$ MOLAR RATIO OF 2.0

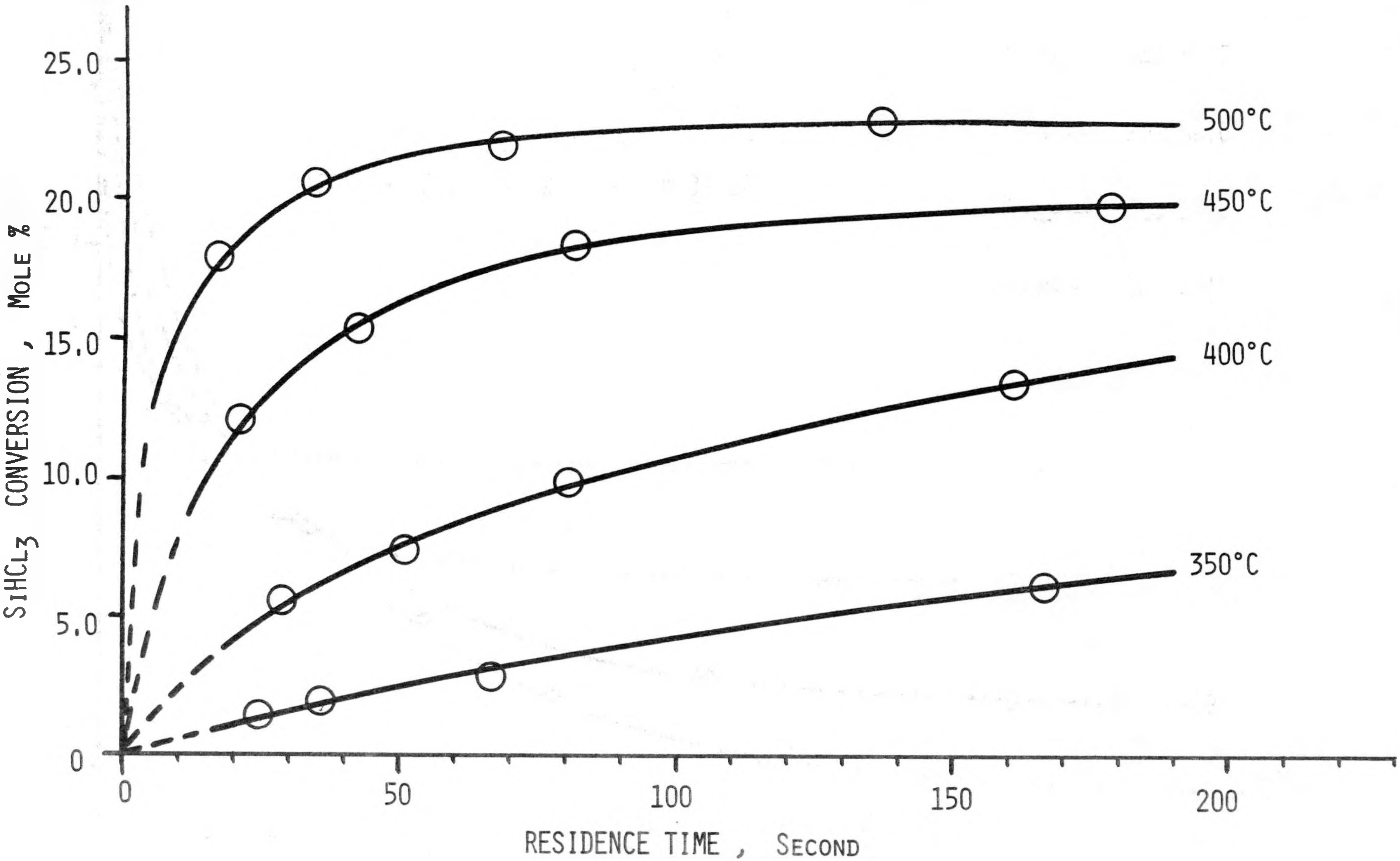
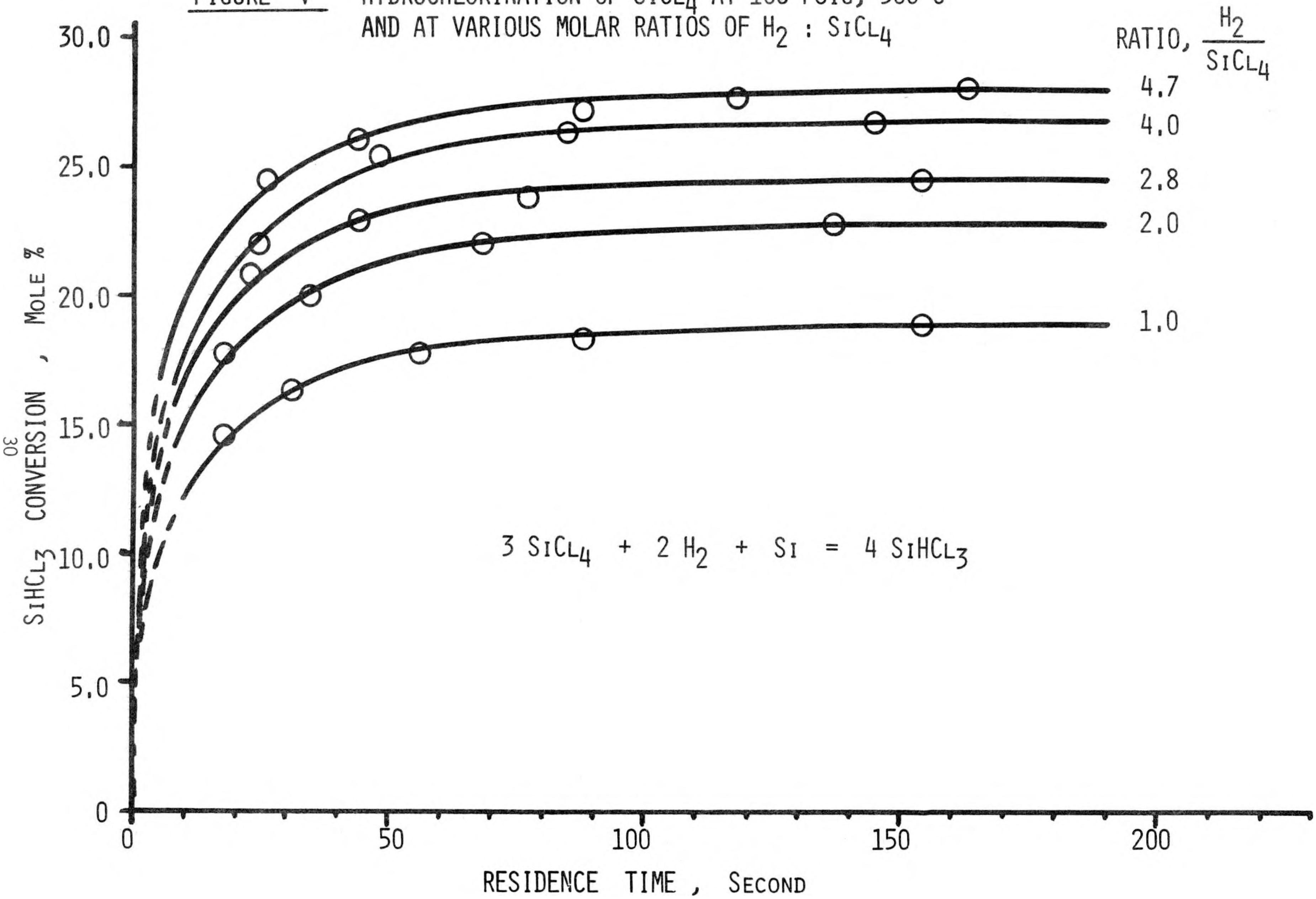


FIGURE V HYDROCHLORINATION OF $SiCl_4$ AT 100 PSIG, 500°C AND AT VARIOUS MOLAR RATIOS OF $H_2 : SiCl_4$



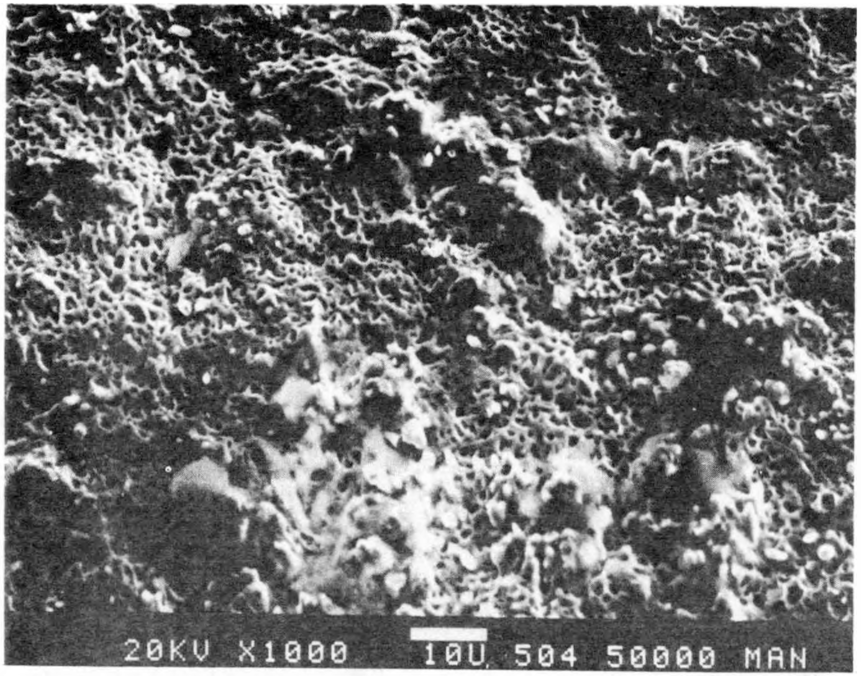
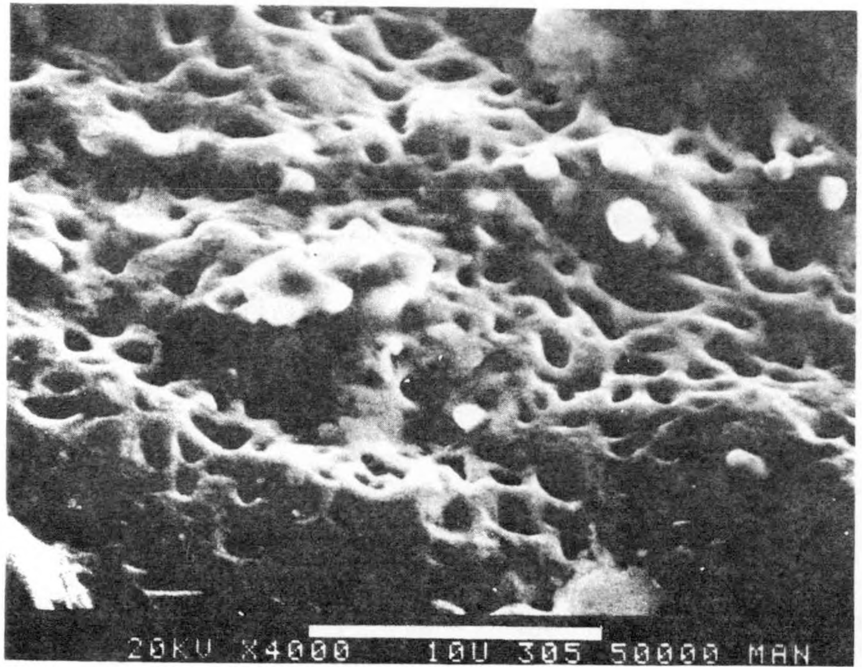


FIGURE VI

CORROSION TEST ON ALLOY 400 (MONEL)
87 HOURS @ 500°C, 300 PSIG, $H_2/SiCl_4 = 2.0$

SCANNING ELECTRON MICROGRAPH OF THE SURFACE OF THE TEST SAMPLE TO SHOW THE MORPHOLOGY OF THE SILICIDE FILM AT VARIOUS MAGNIFICATIONS



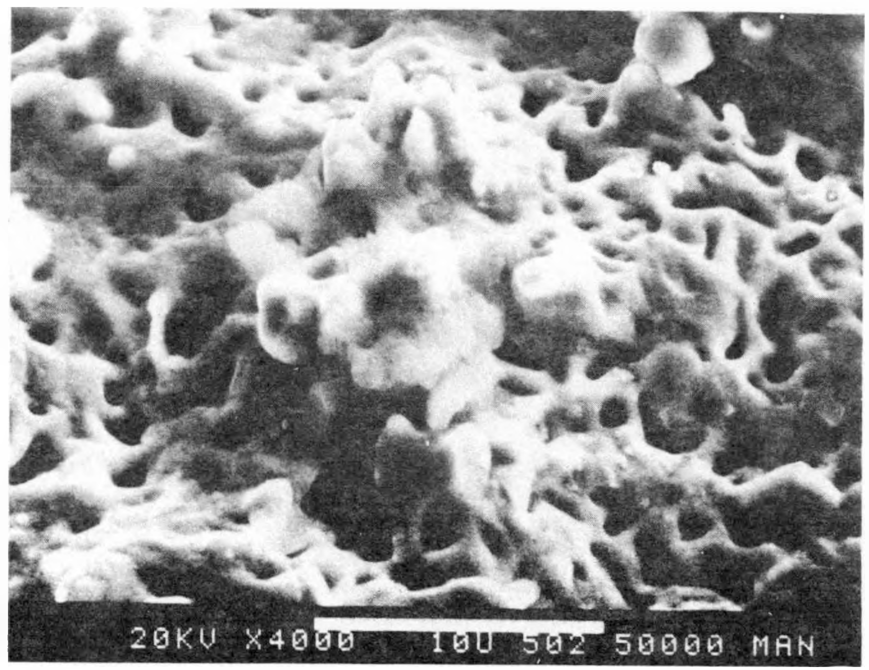
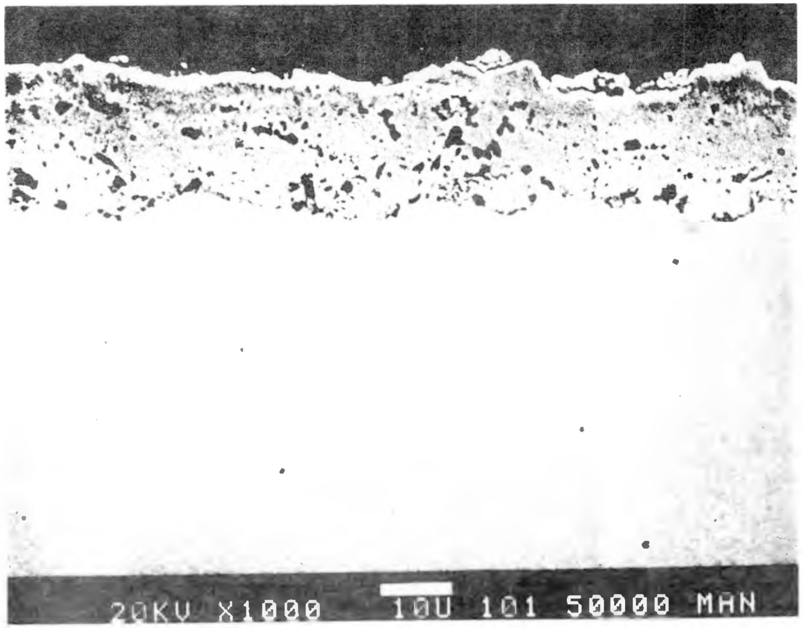
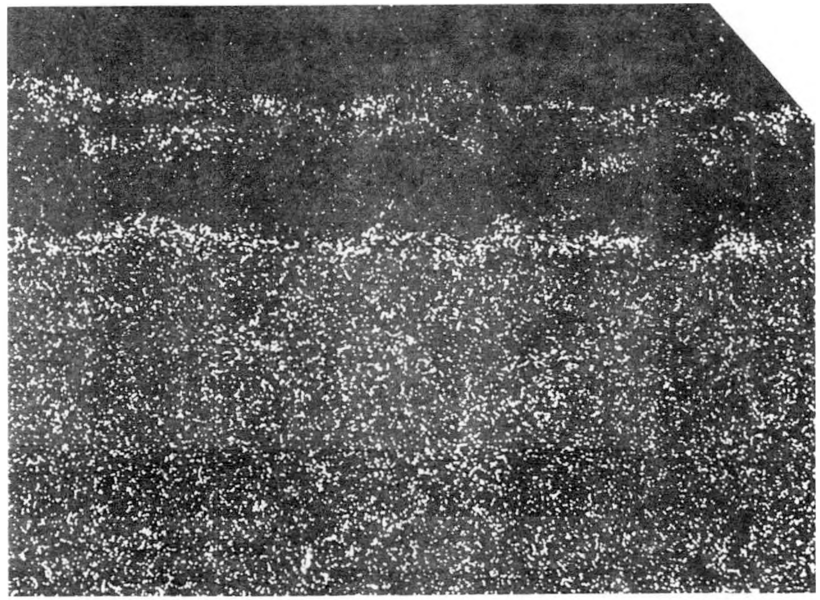


FIGURE VII CORROSION TEST ON ALLOY 400, CROSS SECTIONAL AREA AND X-RAY MAPS

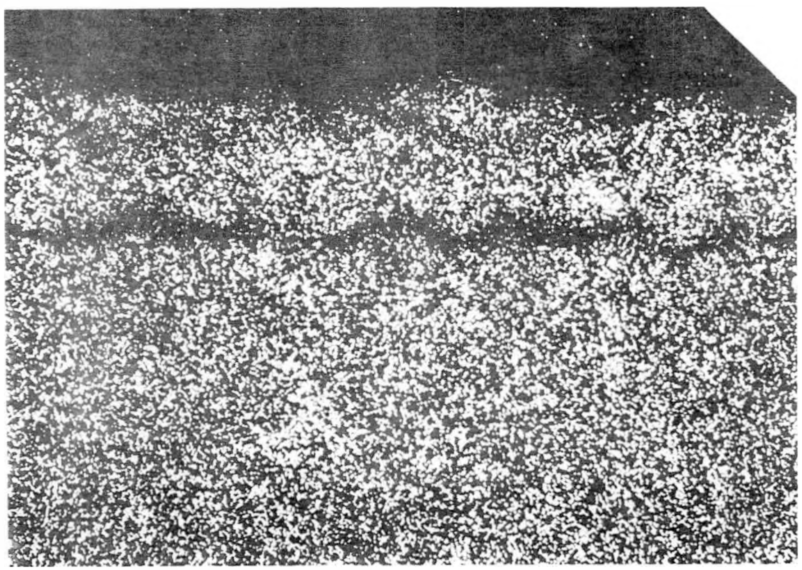


Coating Chemistry Sample # 5 (Silicon over Monel Metal) O.D. Surface

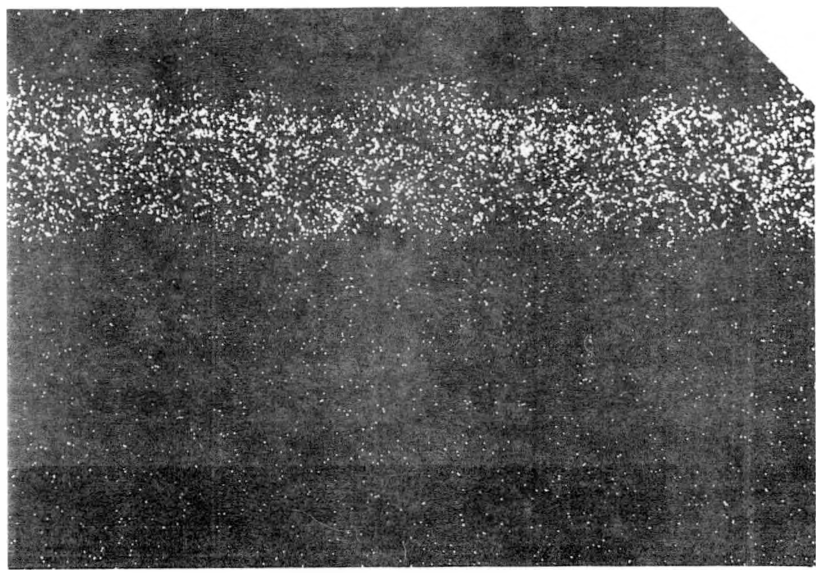


Copper X-ray Distribution

FIGURE 5

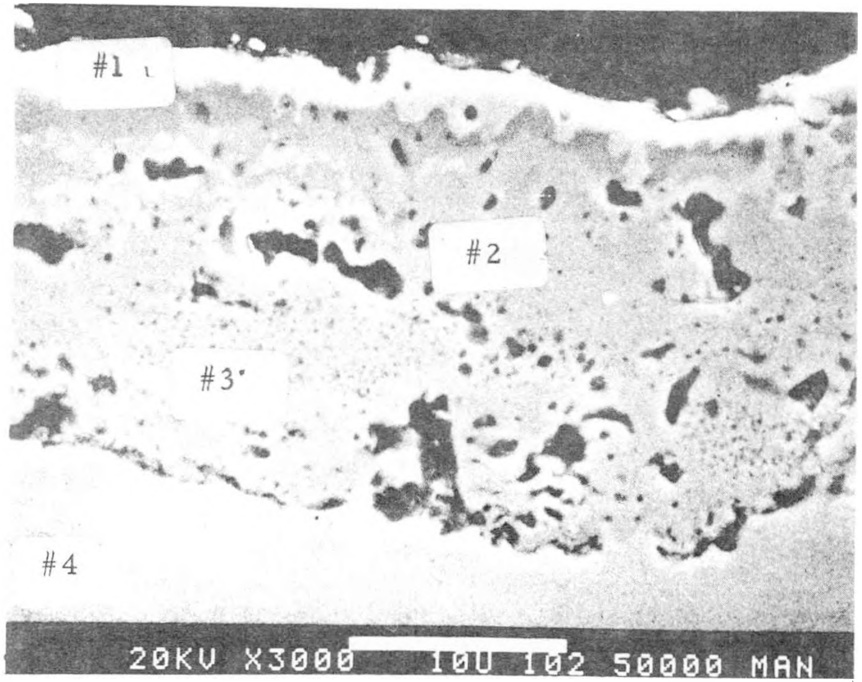


Nickel X-ray Distribution



Silicon X-ray Distribution

<u>FIGURE VIII</u> CORROSION TEST ON ALLOY 400: X-RAY MICROPROBE ANALYSES ON FOUR DIFFERENT AREAS AT THE CROSS SECTION OF THE SAMPLE



5 OD AREA 4
KV=20. TILT=30. TKOFF=29.
BKG PT1= 3.0 BKG PT2=14.0
NOST
21-APR-82

CONCENTRATION

	WT. %	AT. %	% S.E.
SIK	1.11	2.36	8.86
MNK	0.77	0.83	9.23
FEK	1.45	1.55	5.74
NIK	59.86	60.74	0.9[illegible]
CUK	36.81	[illegible]4.52	1.[illegible]

	100.00		

5 OD AREA 1
KV=20. TILT=30. TKOFF=29
BKG PT1= 3.0 BKG PT2=14.0
NOST
21-APR-82

CONCENTRATION

	WT. %	AT. %	% S.E.
SIK	20.52	36.55	1.47
NIK	13.17	11.22	2.17
CUK	66.32	52.22	1.02

	100.00		

5 OD AREA 2
KV=20. TILT=30. TKOFF=29
BKG PT1= 3.0 BKG PT2=14.0
NOST
21-APR-82

CONCENTRATION

	WT. %	AT. %	% S.E.
SIK	24.64	40.88	1.19
FEK	1.76	1.47	5.89
NIK	61.01	48.42	0.92
CUK	12.59	9.24	2.46

	100.00		

5 OD AREA 3
KV=20 TILT=30 TKOFF=29
BKG PT1= 3.0 BKG PT2=14.0
NOST
21-APR-82

CONCENTRATION

	WT. %	AT. %	% S.E.
[illegible]	23.23	38.77	1.25
[illegible]	0.35	0.47	15.92
[illegible]	1.73	1.45	5.15
[illegible]	69.27	55.[illegible]1	0.87
[illegible]	5.41	[illegible].99	4.11

	100.00		

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