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FLAT-PLATE SOLAR ARRAY PROJECT

TASK I SILICON MATERIAL

QUARTERLY REPORT

INVESTIGATION OF THE HYDROCHLORINATION OF $SiCl_4$

(Covering the Period October 1, 1981 to January 8, 1982)

JPL CONTRACT NO. 956061

TO

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

BY

JEFFREY Y. P. MUI

January 9, 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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"Investigation of the Hydrochlorination of $SiCl_4$"

SECOND QUARTERLY REPORT

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ABSTRACT

A new two inch-diameter stainless steel reactor was designed and built to operate at pressures up to 500 psig for the experimental studies on the hydrochlorination of $SiCl_4$ and metallurgical grade (m.g.) silicon metal to $SiHCl_3$,

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

After a thorough safety review, the hydrochlorination reactor system was successfully started-up in the month of December. Preliminary experiments on the hydrochlorination of $SiCl_4$ and m.g. silicon metal were carried out. One experiment was conducted under the same reaction conditions as that carried out previously with the one inch-diameter laboratory reactor. Results of the reaction kinetic measurements with the 2" reactor show good agreement with the previously obtained results.

The effect of pressure on the hydrochlorination reaction was studied. In order to clearly see the effect of pressure, the experiments were carried out at low reactor pressures of 73 psig and 150 psig, respectively. A large pressure effect on

the hydrochlorination reaction was observed between the results of the low pressure experiments and the results of the high pressure experiments. In general, higher pressure produces a higher conversion of $SiHCl_3$ but at a slower reaction rate. The effect of temperature on the hydrochlorination reaction was studied at 73 psig. As previously observed, higher reaction temperature gives both a higher conversion of $SiHCl_3$ and a higher reaction rate.

Samples of the material of construction for the hydrochlorination reactor were prepared for the corrosion study. Materials include Type 304 stainless steel, carbon steel, Incoloy 800H, Alloy 400 (Monel), Hastelloy B-2 (a Ni/Mo alloy), nickel and copper. These test samples were mounted in a stainless steel rack which was fitted inside the 2" reactor tube. The corrosion tests are in progress.

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I. INTRODUCTION

A research and development program was initiated in July of last year to study the hydrochlorination of $SiCl_4$ and m.g. silicon metal to $SiHCl_3$,

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

The concept of hydrochlorination originated from the Union Carbide, silane-to-silicon process, in which the by-product $SiCl_4$ is recycled back to $SiHCl_3$ by its reaction with m.g. silicon metal and hydrogen[1]. The Hemlock Semiconductor polysilicon process based on chemical vapor deposition also utilizes the hydrochlorination reaction to recycle the $SiCl_4$ generated in its SiH_2Cl_2 process[2]. The hydrochlorination reaction has been shown in the previous experimental studies to be an efficient process to produce $SiHCl_3$ in good conversion and in high yield [1,3]. Trichlorosilane is also the most widely used starting material for the production of high purity silicon metal. Presently, polycrystalline silicon metal is produced in the Siemens-type reactors, in which $SiHCl_3$ is reduced by hydrogen gas at high temperatures. The commercial Siemens process produces $SiCl_4$ and HCl as the major by-products. Since the hydrochlorination reaction consumes the by-product $SiCl_4$ while produces the $SiHCl_3$ starting material, it has the potential of a practical commercial process to complete a recycle loop for the Siemens process for the production of polycrystalline silicon metal with substantial savings on raw material cost [3].

The objective of the JPL/Solarelectronics Contract No. 956061 on "Investigation of the Hydrochlorination of $SiCl_4$" is primarily designed 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. Also, new idea and new concept are tested with the ultimate goal to improve the efficiency of the hydrochlorination process. The attached Program Plan includes a comprehensive corrosion study to provide a basic understanding on the mechanism of corrosion inside the hydrochlorination reactor and to select the most suitable material of construction for the hydrochlorination reactor. The fluidization mechanism study is designed to explore reactor design concepts based on the merits of a fluidized-bed or a fixed-bed reactor design. An idea to recycle chloride wastes is also included in the investigation as out-lined in the Program Plan.

Construction and installation of the hydrochlorination apparatus have been completed. Experiments on the hydrochlorination of $SiCl_4$ and m.g. silicon metal were carried out. Results are summarized in the following.

II. DISCUSSION

A. 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 function of the hydrochlorination apparatus were reported in detail in the first Quarterly Report (DOE/JPL 956061-1). Construction and installation of the hydrochlorination apparatus have been completed. Instruments were tested and calibrated. After a thorough safety review, the reactor was successfully started-up in the month of December. Preliminary experiments on the hydrochlorination reaction were carried out.

B. Preliminary Experiments on the Hydrochlorination of $SiCl_4$ and M.G. Silicon Metal

Initially, an experiment on the hydrochlorination of $SiCl_4$ and m.g. silicon metal was repeated in the new 2" reactor under the same reaction conditions as one of the experiment previously carried out in the 1" laboratory reactor [3] at 300 psig, 450°C and $H_2/SiCl_4$ molar ratio of 2.8. The purpose of this experiment is to relate the experimental data obtained from this new 2" reactor design to those obtained previously.

The reactor was initially charged with 862 g. (718 cc) 32xD (32 mesh to dust) m.g. silicon metal. Air inside the hydrochlorination apparatus was first evacuated. It was then pressurized with hydrogen gas. The reactor was heated to reaction temperature of 450°C. A mixture of hydrogen gas and $SiCl_4$ vapor was fed into the reactor at a molar ratio of 2.8. After the reactor system had been stabilized, reaction kinetic measurements were made by measuring the % $SiHCl_3$ conversion as a function of residence time. The $H_2/SiCl_4$ feedrates were varied while samples of the reaction product mixture were withdrawn and analyzed by the in-line gas chromatograph as schematically shown in Figure I. Trichlorosilane and a small amount of dichlorosilane are the only significant products produced in the hydrochlorination reaction. The % $SiHCl_3$ conversion was calculated from the G.C. analyses. The residence time is a function of the $H_2/SiCl_4$ feedrate. It is defined as the time in which the movement of the inlet gaseous mixture passes through an empty reactor tube with a volume equals to the volume of the silicon mass bed. For example, if the feedrate of the gaseous $H_2/SiCl_4$ mixture under the reaction condition of 450°C, 300 psig is 718 cc per minute, the residence time is calculated to be 60 seconds for the 862 g. (718 cc) of silicon metal mass bed inside the hydrochlorination reactor. Here, ideal gas behavior is assumed for the gaseous $H_2/SiCl_4$ mixture.

Results of this experiment are summarized in Table I. Data in Table I are presented in Figure II by plotting the % $SiHCl_3$ conversion versus residence time. Also plotted in the same graph are previously obtained experimental results obtained from the one inch-diameter laboratory reactor [3] under similar reaction conditions. As the results in Figure II indicate, the kinetic curve obtained from the new 2" reactor shows a slightly different profile from that of the 1" reactor. However, the difference is small and the deviations are within experimental error. In conclusion, the reaction kinetic data obtained from the new 2" hydrochlorination reactor design are comparable to those obtained previously.

C. Reaction Kinetic Measurements

(1) Function of Pressure

The two inch-diameter hydrochlorination reactor is designed to operate at pressures up to 500 psig. Since the hydrochlorination of $SiCl_4$ and m.g. silicon metal,

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

results a net volume contraction as $SiHCl_3$ is produced, higher pressure is expected to give a higher equilibrium conversion of $SiHCl_3$. The upper pressure range of 500 psig is an optimum reactor pressure for the hydrochlorination reaction and it is still within the limit of conventional chemical processing equipments[1]. Previously, experimental data at 500 psig and at 300 psig show that the reaction rate is slightly slower at 500 psig than that obtained at 300 psig under the same reaction conditions [3]. In order to clearly see the effect of pressure on the hydrochlorination reaction, experiments were carried out at low reactor pressures of 73 psig and 150 psig respectively. The difference between 500 psig and 300 psig represents a mere 63.5% increase in pressure. On the other hand, a 3½-folded increase in pressure is noted between 300 psig. and 73 psig.

A series of experiments was carried out at 73 psig, 450°C and $H_2/SiCl_4$ feed ratio of 2.8. Results of the experiments are summarized in Table II. Data in Table II are presented in Figure III by plotting the % $SiHCl_3$ conversion versus residence time. Also plotted in the same graph are the reaction kinetic data obtained at 300 psig in Table I. Results in Figure II show the evidence of a large pressure effect on the hydrochlorination reaction. The reaction rate, i.e., the rate at which the hydrochlorination reaction approaches its equilibrium

$SiHCl_3$ conversion, is faster a 73 psig than that obtained at 300 psig. For example, it takes approximately 50 seconds residence time for the hydrochlorination reaction to reach 90% equilibrium conversion of $SiHCl_3$ at 73 psig . On the other hand, about 140 seconds residence time are needed at 300 psig to reach the same 90% equilibrium conversion of $SiHCl_3$. Data in Figure III also clearly show that the higher 300 psig pressure produces a higher $SiHCl_3$ conversion. For example, the equilibrium conversion of $SiHCl_3$ is about 21% at 73 psig. A much higher $SiHCl_3$ conversion of 35% is achievable at 300 psig under the same reaction conditions.

The same experiment was repeated at 150 psig and at the same reaction temperature of 450°C and $H_2/SiCl_4$ ratio of 2.8. Results of this experiment are summarized in Table III. Data in Table III are presented in Figure IV by plotting the % $SiHCl_3$ conversion versus residence time. Also plotted in the same graph are the 73 psig data in Table III. As the results in Figure IV show, the effect of pressure on the hydrochlorination reaction is very much the same. In conclusion, the results of these experiments show that a higher pressure produces a higher $SiHCl_3$ conversion but at a slower reaction rate.

(2) Function of Temperature

The effect of temperature on the hydrochlorination reaction was studied at 73 psig and at $H_2/SiCl_4$ feed ratio of 2.8. A series of experiments was carried out at 500°C. Results are summarized in Table IV. Data in Table IV are presented in Figure V by plotting the % $SiHCl_3$ conversion versus residence time. Also poltted in the same graph are the 450°C data in Table II. Data in Figure V show the large effect of temperature on the hydrochlorination reaction. As previously observed, a higher reaction temperature produces both a higher reaction rate and a higher conversion of $SiHCl_3$.

D. Corrosion Study

Samples of material of construction for the hydrochlorination reactor were prepared for the corrosion study. Material include Type 304 stainless steel, carbon steel, Incoloy 800H (a high Ni, Cr alloy), Alloy 400 (Monel, 2/3 Ni, 1/3 Cu), Hastelloy B-2 (a Ni/Mo alloy), nickel and copper. These test samples were mounted on a stainless steel rack which was fitted inside the 2" hydrochlorination reactor tube. In this manner, all the test samples will be exposed to the same reaction enviroment throughout the test procedure. The corrosion test is planned for about one hundred hours of total reaction time.

E. Summary of Progress

Work on the JPL Contract No. 956061 has progressed close to schedule as outlined in the attached Program Plan. The new 2" hydrochlorination reactor system performed as well as it was designed for. Experimental results on the reaction kinetic measurements obtained from this 2" reactor are comparable to those obtained previously. The effect of pressure on the hydrochlorination reaction was studied in detail. By carrying out experiments at low reactor pressures, large pressure effect on the hydrochlorination reaction was observed in comparison with those obtained at high reactor pressures (300 psig). The effect of temperature on the hydrochlorination reaction was briefly studied at the low reactor pressure of 73 psig. Results are similar to those obtained previously. The reaction kinetic data obtained at these low reactor pressures complement the high pressure data which have already been reported previously [3]. Samples of material of construction for the hydrochlorination reactor were prepared and mounted inside the 2" reactor tube. The corrosion test is in progress.

III. PROJECTED THIRD QUARTER ACTIVITIES

Planned activities for the third quarter (January-

March) include,

- Reaction kinetic measurements with HCl added,
- Mass balance,
- Corrosion studies,
- Design and install the four inch-diameter hydrochlorination reactor.

IV. REFERENCES

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

(2) Quarterly Progress Reports (1 to 6), JPL Contract No. 955533, "Development of a Polysilicon Process Based on Chemical Vapor Deposition", Hemlock Semiconductor Corporation, June, 1981.

(3) 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.

V. APPENDIX

Program Plan
Tables I to IV
Figures I to V

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			
VII By-Product HCl Recycle									▲			
(1) Reaction Kinetics with HCl						~~6~~	7	8	9			
(2) Corrosion Measurement with HCl							7	8	9			
(3) Data Evaluation								8	9			
VIII Fluidization Mechanism Study												▲
(1) Design and Install 4" Reactor								8	9	10		
(2) Safety Review, Start-up									9	10		
(3) Reaction Rate Measurements, Fluidized-Bed, Fixed-Bed										10	11	
(4) Data Evaluation										10	11	
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. M , Solarelectronics, Inc.
July 22,1981.

TABLE I

THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 450°C, 300 PSIG AND $H_2/SiCl_4$ RATIO OF 2.8

Experiment No.	Hydrogen Feedrate SLM(1)	Residence Time Second	Reaction Product Composition Mole %		
			SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	1.0	265	1.257	34.47	64.27
			1.259	34.18	64.56
			(1.258)	(34.33)	(64.41)
2	2.0	133	0.9370	30.44	68.63
			0.9791	31.36	67.66
			(0.9581)	(30.90)	(68.15)
3	2.9	91.7	0.6941	27.06	72.25
			0.6379	27.05	72.31
			(0.6660	(27.06)	(72.28)
4	4.0	66.5	0.4091	23.44	76.15
			0.4634	23.15	76.38
			(0.4363)	(23.30)	(76.26)
5	6.6	40.2	0.3149	17.93	81.76
			0.3044	18.21	81.49
			(0.3097)	(18.07)	(81.63)

(1) SLM = Standard Liter per Minute, at 18°C, 760 mm Hg.

TABLE II

THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON
AT 450°C, 73 PSIG AND $H_2/SiCl_4$ RATIO OF 2.8

Experiment No.	Hydrogen Feedrate SLM (1)	Residence Time Second	Reaction Product Composition Mole %		
			SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	0.6	121	0.2659	20.29	79.44
			0.2973	20.61	79.09
			(0.2816)	(20.45)	(79.27)
2	1.2	60.7	0.2595	19.52	80.22
			0.2981	19.40	80.30
			(0.2788)	(19.46)	(80.26)
3	2.15	33.8	0.2294	17.99	81.78
			0.1620	17.54	82.29
			(0.1724)	(17.77)	(82.03)
4	4.4	16.5	0.1635	14.75	85.09
			0.1636	14.91	84.93
			(0.1636)	(14.83)	(85.01)

(1) SLM = Standard Liter per Minute, at 18°C, 760 mm Hg.

TABLE III

THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON

AT 450°C, 150 PSIG AND $H_2/SiCl_4$ RATIO OF 2.8

Experiment No.	Hydrogen Feedrate SLM (1)	Residence Time Second	Reaction Product Composition Mole % SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	0.7	193	0.5577	26.05	73.39
			0.5736	26.07	73.35
			(0.5656)	(26.06)	(73.37)
2	1.25	108	0.3498	21.99	77.66
			0.4398	22.81	76.75
			(0.3948)	(22.40)	(77.21)
3	2.1	64.3	0.3343	20.13	79.54
			0.3626	20.52	79.12
			(0.3485)	(20.33)	(79.33)
4	3.0	45.0	0.2119	16.08	83.70
			0.2347	16.29	83.48
			(0.2233)	(16.19)	(83.59)
5	6.0	22.5	0.1640	12.17	87.66
			0.1689	12.20	87.63
			(0.1665)	(12.19)	(87.65)

(1) SLM = Standard Liter per Minute, at 18°C, 760 mm Hg.

TABLE IV

THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON
AT 500°C, 73 PSIG AND $H_2/SiCl_4$ RATIO OF 2.8

Experiment No.	Hydrogen Feedrate SLM (1)	Residence Time Second	Reaction Product Composition Mole % SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	0.35	193	0.4121	23.51	76.08
			0.3809	24.02	75.60
			(0.3965)	(23.77)	(75.84)
2	0.75	90.1	0.3424	22.36	77.30
			0.3447	22.45	77.21
			(0.3436)	(22.41)	(77.26)
3	1.3	52.0	0.3666	21.68	77.96
			0.3969	22.87	76.73
			(0.3818)	(22.28)	(77.35)
4	2.3	29.4	0.4244	21.44	78.14
			0.4548	21.52	78.02
			(0.4396)	(21.48)	(78.08)
5	4.3	15.7	0.3002	20.02	79.68
			0.3075	19.89	79.80
			(0.3039)	(19.96)	(79.74)

(1) SLM = Standard Liter per Minute, at 18°C, 760 mm Hg.

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

(DRAWING NOT TO SCALE)

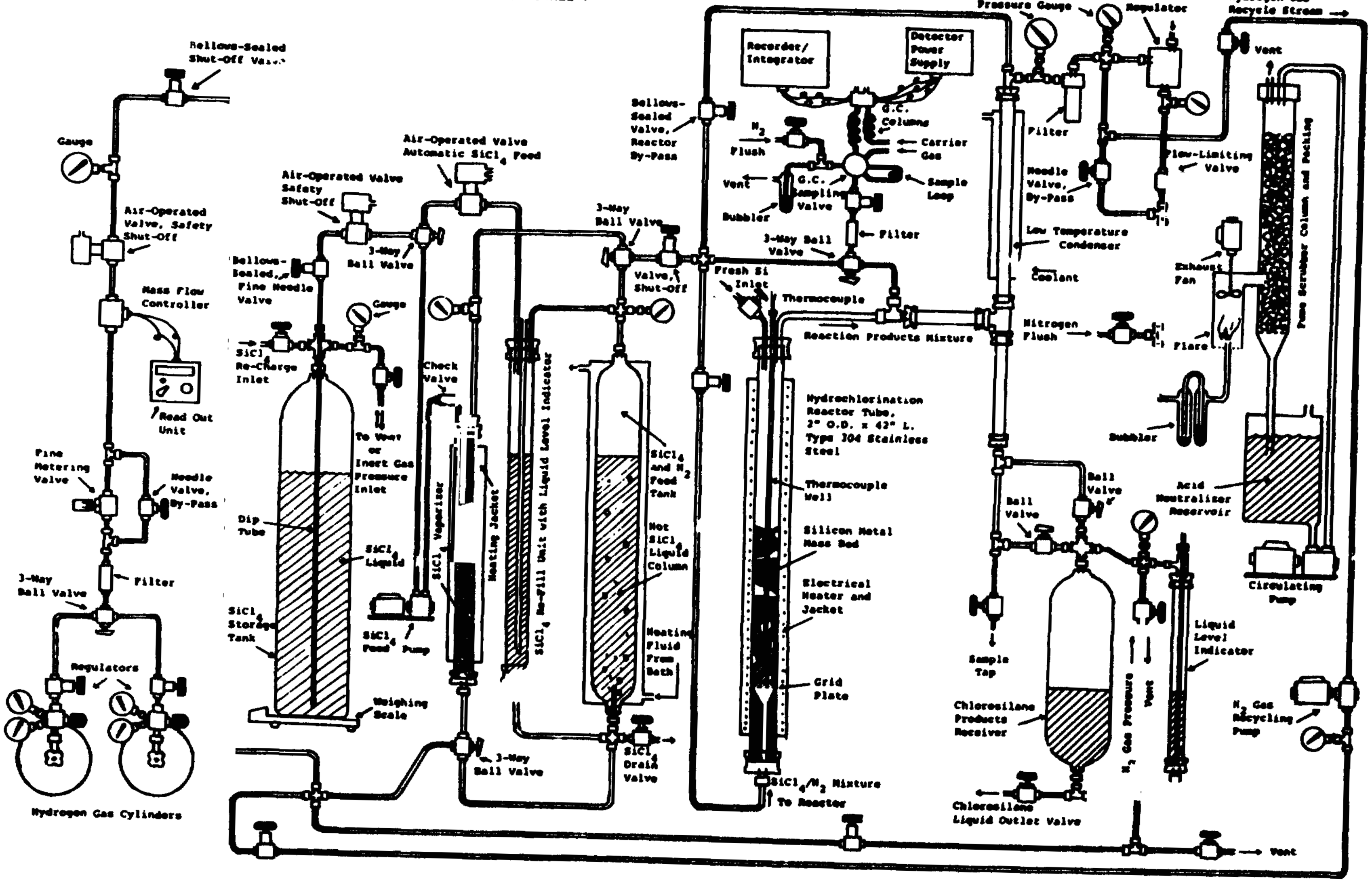

FIGURE II THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON TO $SiHCl_3$ AT 300 PSIG, 450° C AND $H_2/SiCl_4$ MOLAR RATIO OF 2.8

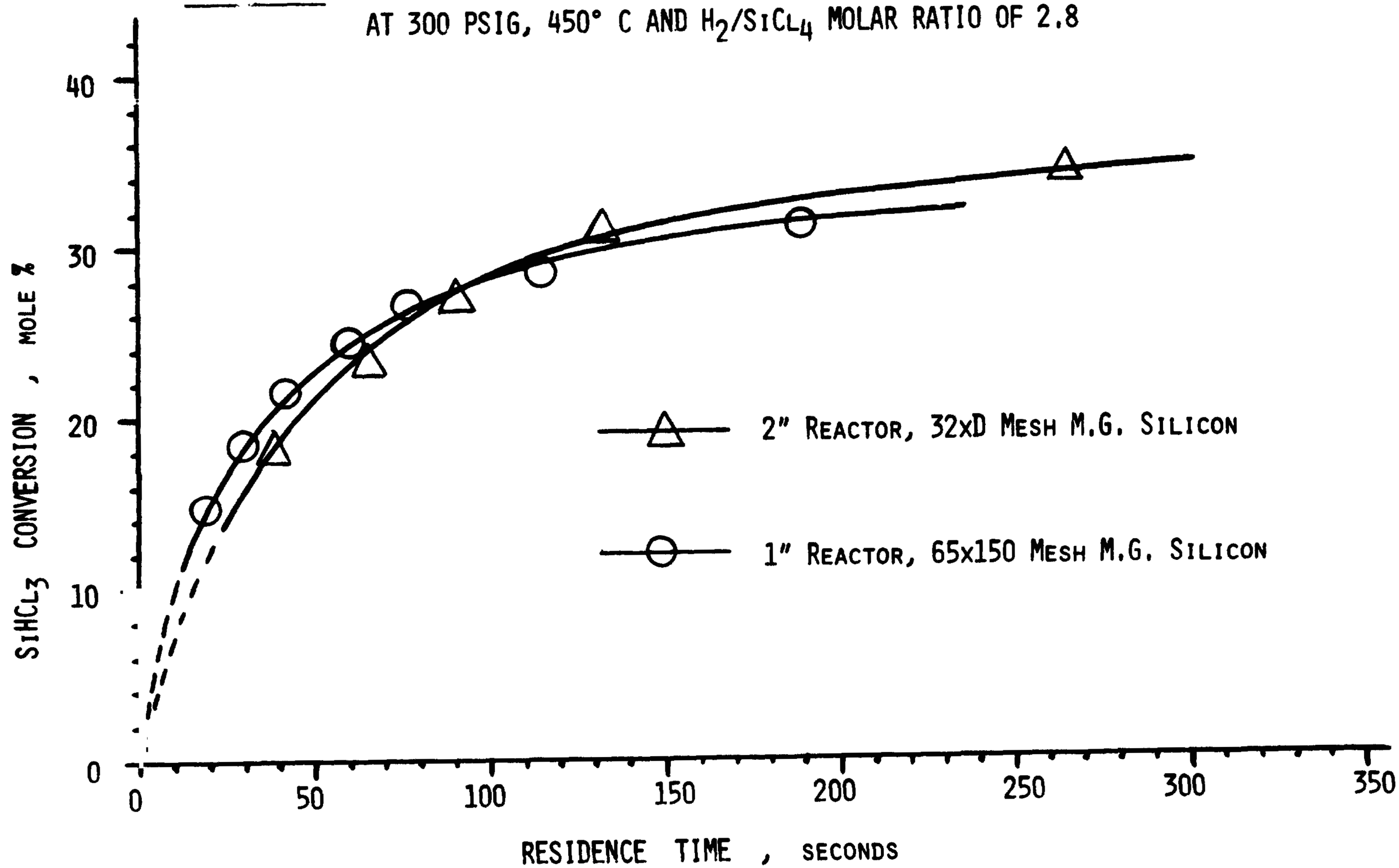

FIGURE III THE EFFECT OF PRESSURE ON THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 450°C AND $H_2/SiCl_4$ RATIO OF 2.8

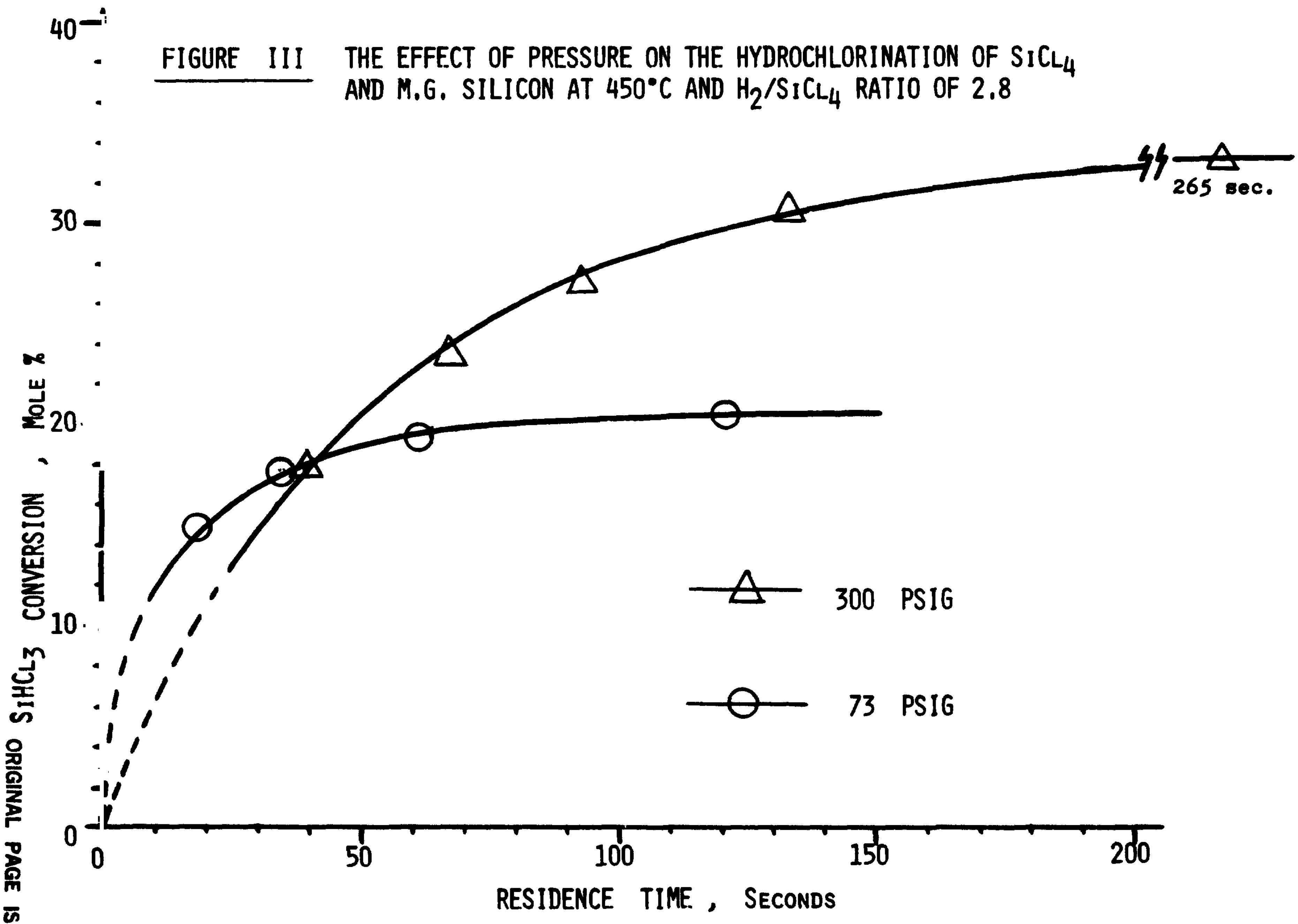

FIGURE IV THE EFFECT OF PRESSURE ON THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 450°C AND $H_2/SiCl_4$ RATIO OF 2.8

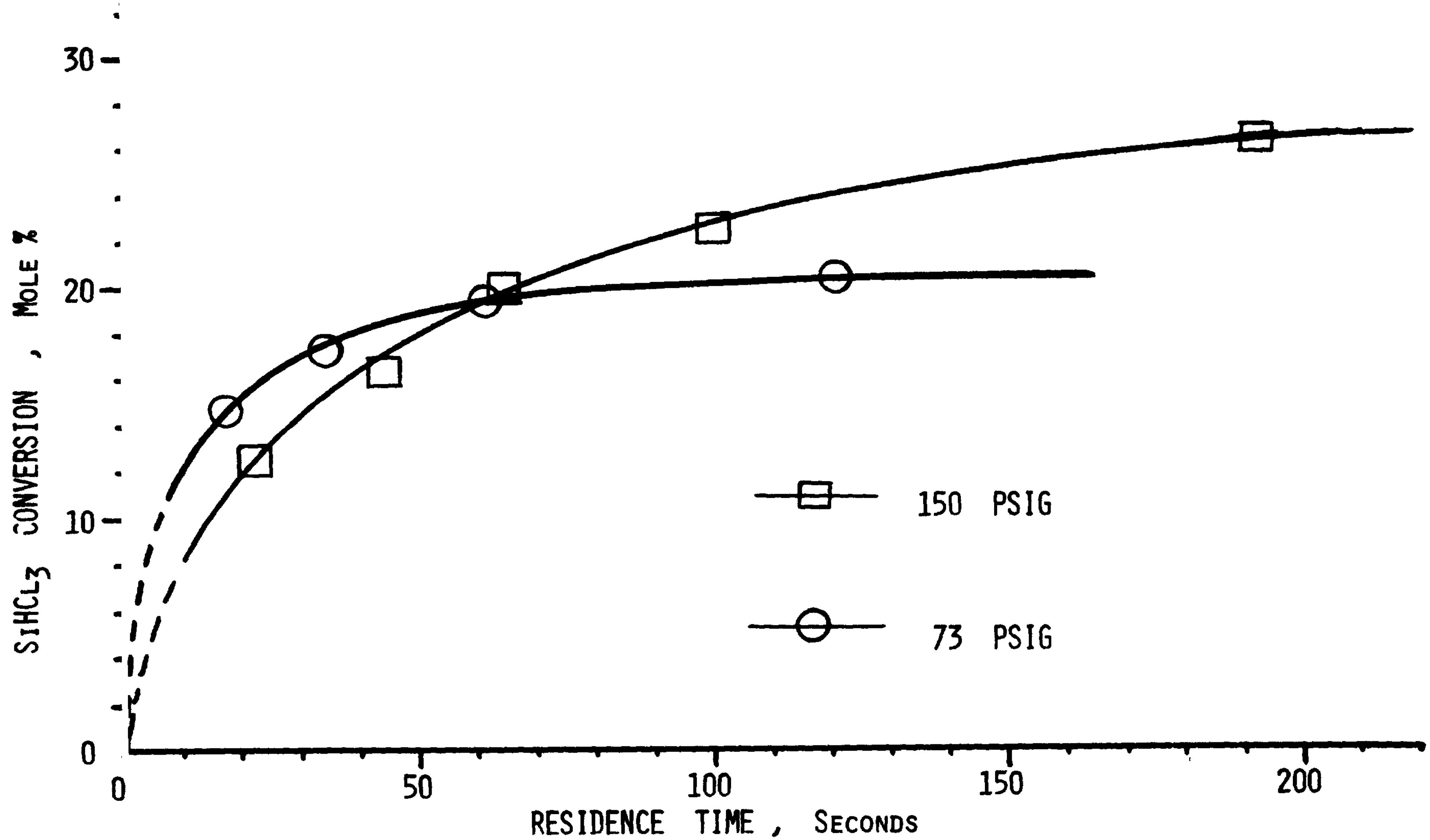

FIGURE V THE EFFECT OF TEMPERATURE ON THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 73 PSIG AND $H_2/SiCl_4$ MOLAR RATIO OF 2.8