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DOE/JPL/955382-79/8
(DE81025543)

INVESTIGATION OF THE HYDROGENATION OF $SiCl_4$

Final Report for the Period March 31, 1979—April 1, 1981

Low-Cost Solar Array Project Silicon Material Task

By
Jeffrey Y. P. Mui
Dietmar Seyferth

MASTER

April 15, 1981

Work Performed Under Contract No. NAS-7-100-955382

Massachusetts Institute of Technology
Cambridge, Massachusetts

U.S. Department of Energy

Solar Energy

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Price: Printed Copy A06
Microfiche A01

DOE/JPL/955382-79/8
(DE81025543)
Distribution Category UC-63b

FINAL REPORT

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JPL Contract No. 955 382

April 15, 1981

Low-Cost Solar Array Project
Silicon Material Task

to
Jet Propulsion Laboratory
California Institute of Technology

by

JEFFREY Y.P. MUI

DIETMAR SEYFERTH

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
OFFICE OF SPONSORED PROGRAMS
DEPARTMENT OF CHEMISTRY
CAMBRIDGE, MASSACHUSETTS 02139

The JPL Low-Cost Silicon 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 perfomed for the Jet Propulsion Laboratory, California Institute of Technology, by agreement between NASA and DOE.

LOW-COST SOLAR ARRAY PROJECT

SILICON MATERIAL TASK

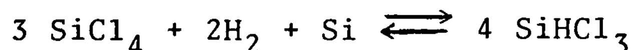
"Investigation of the Hydrogenation of $SiCl_4$"

Jeffrey Y.P. Mui*
Dietmar Seyferth

Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

ABSTRACT

A two-year research and development program was initiated in April of 1979 to study the hydrochlorination of silicon tetrachloride and metallurgical grade (m.g.) silicon metal to trichlorosilane,



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

This complementary research and development effort is conducted to supplement the engineering process development activities for the Experimental Process System Development Unit (EPSDU) under the Union Carbide Contract No. 954 334 of the JPL Low-Cost Solar Array (LSA) Project. A laboratory scale pressure reactor was constructed to study this

*Present Address: Solarelectronics, Inc. 21 Rita Lane, P.O. Box 141, Bellingham, Massachusetts 02019

reaction at pressures up to 500 psig. Reaction kinetic measurements were carried out as a function of reactor pressure, reaction temperature and $H_2/SiCl_4$ feed ratio. The conditions for reaction kinetic data collected at 500 psig were specifically designed to complement the engineering design for the hydrochlorination reactor in the Union Carbide EPSDU, silane-to-silicon process.

The effect of an added copper catalyst on the reaction rate was investigated. The presence of a 2 wt% copper catalyst approximately increases the reaction rate by a factor of two. Different particle size distributions of the m.g. silicon metal were utilized to study the effect of total solid surface area on the rate of the hydrochlorination reaction. Interestingly, the reaction rate was found to be essentially constant within a particle size range of -30 mesh to +400 mesh. The effect of impurities in the m.g. silicon appeared to act like a catalyst to greatly increase the rate of the hydrochlorination reaction. Experiments were carried out with the object to study the life of the silicon mass bed with and without the presence of a copper catalyst. The effect of a prolonged reaction on the reaction rate was investigated. No significant change in the rate of reaction was observed after several hundred hours of reaction. The longevity of the Si mass bed is an important factor to operate the hydrochlorination process efficiently and economically. A corrosion study was made on

type 304 stainless steel and Incoloy 800H under the actual hydrochlorination reaction environment. A silicide protective film was formed at the reactor wall. The presence of such a silicide film protected the metal reactor from the corrosive environment of the hydrochlorination reaction.

Based on the reaction kinetic data, the hydrochlorination of $SiCl_4$ and m.g. silicon metal is found to be an efficient process to produce $SiHCl_3$ in good conversions and in high yields. Copper is an effective catalyst. Results of the corrosion study show that conventional nickel-chromium alloys are suitable material of construction for the hydrochlorination reactor. The hydrochlorination reaction is relatively insensitive to external process parameters such as silicon particle size distribution and and the impurities in the m.g. silicon metal. These are advantageous factors since they provide a broad process lattitude for the engineering design of the hydrochlorination reactor. The hydrochlorination reaction of $SiCl_4$ and m.g. silicon is an important reaction step to provide a closed-loop process in recycling the by-product $SiCl_4$ and hydrogen in the Union Carbide silane-to-silicon process. It is also a potentially viable commercial process for the production of $SiHCl_3$. For example, it can be incorporated into a closed-loop scheme for the Siemens Process for the production of poly-crystalline silicon metal with a substantial savings on the raw material cost.

TABLE OF CONTENTS

	Page No.
ABSTRACT	i
TABLE OF CONTENTS	iv
I. SUMMARY	1
II. INTRODUCTION	5
III. DISCUSSIONS	6
A. The Hydrochlorination Apparatus	7
B. The In-Line Gas Chromatograph	10
C. Reaction Kinetic Measurements	11
(1) Function of Temperature	13
(2) Function of $H_2/SiCl_4$ Ratio	15
(3) Function of Pressure	16
D. Copper Catalyst Studies	18
(1) Cement Type Copper	18
(2) Cuprous Chloride	21
(3) Effect of Copper Catalyst Concentration on the Reaction Rate	23
(4) Reaction Mechanism and the Role of Copper	25
E. Silicon Particle Size Distribution	30
F. Effect of Impurities in the m.g. Silicon Metal	32
G. Mass Life Studies	35
(1) Effect of a Prolonged Reaction on the Reaction Rate	37
(2) Material Balance on Silicon	40
(3) Distribution of Impurities in the Elutriated Fines	41
H. Corrosion Studies	43
IV. CONCLUSIONS	51
V. RECOMMENDATIONS	54
(1) Optimum Process Parameters	54
(2) Additional Work for the Hydrochlorination Process	55
(3) A Closed-Loop Concept for the Siemens Process	56

Page No.

VI. REFERENCES 59

VII. APPENDICES 59

TABLE I, HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 500 PSIG, 500°C, $H_2/SiCl_4$ = 2.8

TABLE II, HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 500 PSIG, 450°C, $H_2/SiCl_4$ = 2.8

TABLE III, HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 500 PSIG, 550°C, $H_2/SiCl_4$ = 2.8

TABLE IV, HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 300 PSIG, 500°C, $H_2/SiCl_4$ = 1.0

TABLE V, HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 300 PSIG, 500°C, $H_2/SiCl_4$ = 1.0

TABLE VI, HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 300 PSIG, 450°C, $H_2/SiCl_4$ = 1.0

TABLE VII, HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 300 PSIG, 400°C, $H_2/SiCl_4$ = 1.0

TABLE VIII, HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 300 PSIG, 500°C, $H_2/SiCl_4$ = 2.8

TABLE IX, HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 300 PSIG, 450°C, $H_2/SiCl_4$ = 2.8

TABLE X, HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 300 PSIG, 400°C, $H_2/SiCl_4$ = 2.8

TABLE XI, HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 500 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 2.8 WITH 5% CEMENT COPPER

TABLE XII, HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 500 PSIG, 450°C AND $H_2/SiCl_4$ RATIO OF 2.8 WITH 5% CEMENT COPPER

TABLE XIII, HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 300 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 1.0 WITH 5% CEMENT COPPER

TABLE XIV, HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 300 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 2.8 WITH 5% CEMENT COOPER

TABLE XV, HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 500 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 2.8 WITH 5% CUPROUS CHLORIDE

TABLE XVI, HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 500 PSIG, 450°C AND $H_2/SiCl_4$ RATIO OF 2.8 WITH 5% CUPROUS CHLORIDE

TABLE XVII, HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 300 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 1.0 WITH 5% CUPROUS CHLORIDE

TABLE XVIII, HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 300 PSIG, 400°C AND $H_2/SiCl_4$ RATIO OF 1.0 WITH 5% CUPROUS CHLORIDE

TABLE XIX, HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 300 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 1.0 WITH 2% CUPROUS CHLORIDE

TABLE XX, PARTICLE SIZE DISTRIBUTIONS OF M.G. SILICON METAL FOR THE HYDROCHLORINATION STUDIES

TABLE XXI, HYDROCHLORINATION OF $SiCl_4$ AND 32 x 65 MESH M.G. SILICON AT 500 PSIG, 500°C AND $H_2/SiCl_4$ = 2.8

TABLE XXII, HYDROCHLORINATION OF $SiCl_4$ AND 150 x 400 MESH M.G. SILICON AT 500 PSIG, 500°C AND $H_2/SiCl_4$ = 2.8

TABLE XXIII, HYDROCHLORINATION OF $SiCl_4$ AND 150 x 400 MESH M.G. SILICON AT 300 PSIG, 500°C AND $H_2/SiCl_4$ = 1.0

TABLE XXIV, HYDROCHLORINATION OF $SiCl_4$ AND 32 x 65 MESH M.G. SILICON AT 300 PSIG, 500°C AND $H_2/SiCl_4$ = 1.0

TABLE XXV, HYDROCHLORINATION OF $SiCl_4$ AND ELECTRONIC GRADE SILICON AT 500 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 2.8

TABLE XXVI, HYDROCHLORINATION OF $SiCl_4$ AND ELECTRONIC GRADE SILICON AT 500 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 2.8 WITH 5% CuCl ADDED

TABLE XXVII, SELECTED KINETIC DATA FROM A PROLONGED HYDROCHLORINATION REACTION AT 300 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 2.0

FIGURE I, THE HYDROCHLORINATION APPARATUS

FIGURE II, $H_2/SiCl_4$ FEED INLET TO REACTOR AND GRID DESIGN

FIGURE III, HYDROCHLORINATION REACTION RATE AT 500 PSIG AND $H_2/SiCl_4$ RATIO OF 2.8 AS A FUNCTION OF TEMPERATURE

FIGURE IV, HYDROCHLORINATION REACTION RATE AT 300 PSIG AND $H_2/SiCl_4$ RATIO OF 1.0 AS A FUNCTION OF TEMPERATURE

FIGURE V, HYDROCHLORINATION REACTION RATE AT 300 PSIG AND $H_2/SiCl_4$ RATIO OF 2.8 AS A FUNCTION OF TEMPERATURE

FIGURE VI, HYDROCHLORINATION REACTION RATE AT 300 PSIG AND 500°C AS A FUNCTION OF $H_2/SiCl_4$ RATIO

FIGURE VII, EFFECT OF REACTOR PRESSURE ON THE HYDROCHLORINATION REACTION RATE AT 450°C AND $H_2/SiCl_4$ RATIO OF 2.8

FIGURE VIII, EFFECT OF REACTOR PRESSURE ON THE HYDROCHLORINATION REACTION RATE AT 500°C AND $H_2/SiCl_4$ RATIO OF 2.8

FIGURE IX, HYDROCHLORINATION REACTION RATE AT 300 PSIG, 500°C AND $H_2/SiCl_4$ = 1.0 WITH 5% CEMENT COPPER AS A FUNCTION OF REACTION TIME

FIGURE X, HYDROCHLORINATION REACTION RATE AT 500 PSIG, 500°C AND $H_2/SiCl_4$ = 2.8 WITH 5% CEMENT COPPER

FIGURE XI HYDROCHLORINATION REACTION RATE AT 500 PSIG, 450°C AND $H_2/SiCl_4$ = 2.8 WITH 5% CEMENT COPPER

FIGURE XII, HYDROCHLORINATION REACTION RATE AT 300 PSIG, 500°C AND $H_2/SiCl_4$ = 1.0 WITH 5% CEMENT COPPER

FIGURE XIII, HYDROCHLORINATION REACTION RATE AT 300 PSIG, 500°C AND $H_2/SiCl_4$ = 2.8 WITH 5% CEMENT COPPER

FIGURE XIV, HYDROCHLORINATION REACTION RATE AT 300 PSIG, 500°C AND $H_2/SiCl_4$ = 1.0 WITH 5% CuCl

FIGURE XV, HYDROCHLORINATION REACTION RATE AT 500 PSIG, 500°C AND $H_2/SiCl_4$ = 2.8 WITH 5% CuCl

FIGURE XVI, HYDROCHLORINATION REACTION RATE AT 500 PSIG, 450°C AND $H_2/SiCl_4$ = 2.8 WITH 5% CuCl

FIGURE XVII, HYDROCHLORINATION REACTION RATE AT 300 PSIG, 500°C AND $H_2/SiCl_4$ = 1.0 WITH 5% CuCl

FIGURE XVIII, HYDROCHLORINATION REACTION RATE AT 300 PSIG, 400°C AND $H_2/SiCl_4$ = 1.0 WITH 5% CuCl

FIGURE XIX, HYDROCHLORINATION REACTION RATE AT 300 PSIG, 500°C AND $H_2/SiCl_4$ = 1.0 WITH 2% CuCl

FIGURE XX, EFFECT OF COPPER CATALYST CONCENTRATION ON THE HYDROCHLORINATION REACTION RATE AT 300 PSIG, 500°C AND $H_2/SiCl_4$ = 1.0

FIGURE XXI, REACTIVITIES OF CEMENT COPPER AND CUPROUS CHLORIDE IN THE HYDROCHLORINATION REACTION

FIGURE XXII, HYDROCHLORINATION REACTION RATE AT 500 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 2.8 AS A FUNCTION OF Si PARTICLE SIZE DISTRIBUTIONS

FIGURE XXIII, HYDROCHLORINATION REACTION RATE AT 300 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 1.0 AS A FUNCTION OF Si PARTICLE SIZE DISTRIBUTIONS

FIGURE XXIV, HYDROCHLORINATION REACTION RATE WITH ELECTRONIC GRADE Si AT 500 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 2.8

FIGURE XXV, HYDROCHLORINATION REACTION RATE WITH ELECTRONIC GRADE Si AT 500 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 2.8 WITH 5% CuCl ADDED.

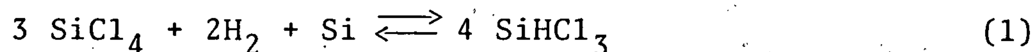
FIGURE XXVI, EFFECT OF PROLONGED REACTIONS ON THE HYDROCHLORINATION REACTION RATE AT 500°C, 300 PSIG, AND $H_2/SiCl_4$ RATIO OF 2.0 WITH AND WITHOUT COPPER CATALYST ADDED

FIGURE XXVII, SCHEMATIC DRAWING OF THE INCOLOY 800H TEST SAMPLE

FIGURE XXVIII, SCHEMATIC DIAGRAM OF A CLOSED-LOOP CONCEPT FOR THE SIEMENS PROCESS

I. SUMMARY

The two-year research and development at the Massachusetts Institute of Technology (JPL Contract No. 955382) on "The Hydrogenation of Silicon Tetrachloride" was conducted primarily as a complentary effort to supplement the engineering process development activities for the Union Carbide silane-to-silicon process. Two parallel efforts were carried out to study the hydrochlorination of $SiCl_4$ and m.g. silicon metal for producing $SiHCl_3$,



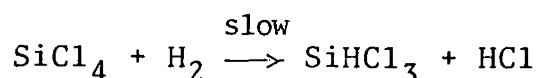
$$3\ SiCl_4 + 2H_2 + Si \rightleftharpoons 4\ SiHCl_3 \tag{1}$$

One was to collect reaction kinetic data as a function of pressure, temperature and $H_2/SiCl_4$ feed ratio, as well as other important process parameters, such as copper catalyst, particle size distribution, impurities in m.g. silicon, Si mass bed life and corrosion effect. The other parallel effort was oriented toward basic research with an attempt to understand the mechanism of the hydrochlorination reaction and the nature of the copper catalyst. A laboratory pressure reactor was designed to operate at 500 psig. The conditions for the collection of the reaction kinetic data at this pressure is specifically designed to complement the engineering design of the hydrochlorination reactor in the Union Carbide EPSDU, which is proposed to operate at 500 psig. Previously, experimental data on the hydrochlorination reaction were collected at reactor

pressure only up to 200 psig. The results of the reaction rate measurements show a large effect of reaction temperature. As previously observed, higher reaction temperature produces a rapid increase of the reaction rate. The effect of reactor pressures on the hydrochlorination reaction shows a somewhat slower reaction rate at 500 psig at short residence times in comparison with those obtained at 300 psig. However, as the reaction approaches equilibrium at longer residence times, the reaction rate measured as a function of $SiHCl_3$ conversion becomes higher at 500 psig in comparison with those obtained at a lower reactor pressure of 300 psig. This observation is in agreement with the thermodynamic function of the hydrochlorination reaction (Equation 1) which results in a net volume contraction as product $SiHCl_3$ is produced. At higher $H_2/SiCl_4$ feed ratio, the conversion of $SiHCl_3$ increases. This is expected since an increase in the partial pressure of hydrogen in Equation (1) drives the equilibrium of the hydrochlorination reaction to the right hand side to produce more $SiHCl_3$.

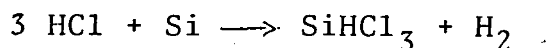
Copper is an effective catalyst for the hydrochlorination of $SiCl_4$ and m.g. silicon metal to $SiHCl_3$. The presence of a copper catalyst approximately doubles the reaction rate. The copper catalyst study provides some experimental evidence of the nature of catalytic sites. The active catalytic species

of copper is in the form of Cu-Si alloys on the silicon metal surfaces. The reaction mechanism is postulated as a gas-solid reaction. The reduction of adsorbed $SiCl_4$ by hydrogen at the active sites on the Si metal surface is the slow, rate-determining step,



$$SiCl_4 + H_2 \xrightarrow{\text{slow}} SiHCl_3 + HCl$$

This is followed by a fast reaction of HCl with silicon on the metal surface to produce more $SiHCl_3$,



$$3\ HCl + Si \longrightarrow SiHCl_3 + H_2$$

This mechanism is also in agreement with the results obtained from the silicon particle size distribution studies. The reaction rate is independent of the Si particle size with a range of -30 mesh to +400 mesh. (510 to 46 microns). These results show that the chemical reaction occuring on the solid surface is the rate-determining step, while mass transfer via diffusion is not rate-limiting. The effect of impurities in the m.g. silicon metal was investigated. Experiments carried out with an ultra-pure, electronic grade silicon metal show a much slower reaction rate in comparison with those obtained with the impure m.g. silicon metal. The metallic impurities on the silicon metal surface function like a catalyst. The catalytic activities of copper and these metallic impurities are postulated as crystal defects caused by the presence of these foreign atoms in the silicon crystal lattic.

The effect of a prolonged reaction on the hydrochlorination of $SiCl_4$ and m.g. silicon was studied. No significant change in the reaction rate is observed after several hundred hours of reaction. The Si mass bed appears to have a long mass life. The longevity of the Si mass bed is an important factor in operating the hydrochlorination process efficiently and economically. A corrosion study was made on Type 304 stainless steel and Incoloy 800H. The results of the corrosion studies showed no significant amount of corrosion on the metal reactor tube. A protective silicide film is formed at the reactor wall under the hydrochlorination reaction conditions. The presence of such a silicide film protects the metal reactor wall from the reaction environment. The serious corrosion problems cited in the earlier report by Union Carbide is most likely due to a secondary atmospheric corrosion and not due to the hydrochlorination reaction itself.

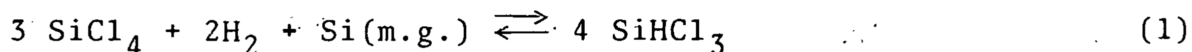
In conclusion, the hydrochlorinatwon of $SiCl_4$ and m.g. silicon metal is an efficient reaction to produce high yield and good conversion of $SiHCl_3$. It is an important step to complete the recycle loop in the Union Carbide silane-to-silicon process. The hydrochlorination reaction provides an efficient process scheme to recycle $SiCl_4$ to $SiHCl_3$. It fits perfectly into the concept of a closed-loop process for the Siemens type reactors currently used in the electronics industry for the production of polycrystalline silicon metal with significant

savings in raw material cost. From a process and from an economics point of view, the hydrochlorination reaction is potentially a practical process for the commercial production of trichlorosilane.

II INTRODUCTION

The MIT Contract No. 955 382 is part ot the Silicon Material Task under the Low-Cost Solar Array Project managed by the Jet Propulsion Laboratory, California Institute of Technology. This two-years research and development contract covered the period from March 31, 1979 to April 1, 1981.

The hydrochlorination of $SiCl_4$ and m.g. silicon metal is the front end step in the Union Carbide Silane-to-silicon process represented by the following reaction sequences.



$$3\ SiCl_4 + 2H_2 + Si(m.g.) \rightleftharpoons 4\ SiHCl_3 \tag{1}$$

$$2\ SiHCl_3 \rightleftharpoons SiCl_4 + SiH_2Cl_2 \tag{2}$$

$$3\ SiH_2Cl_2 \rightleftharpoons 2\ SiHCl_3 + SiH_4 \tag{3}$$

$$SiH_4 \xrightarrow{\Delta} 2H_2 + Si(Solar) \tag{4}$$

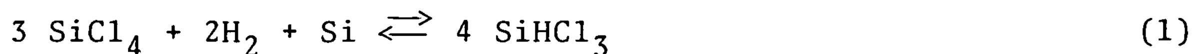
The hydrochlorination reaction (Equation 1) completes the closed loop process scheme by recycling the by-products, $SiCl_4$ and hydrogen. The overall reaction becomes merely a purification scheme to convert impure metallurgical grade (m.g.) silicon metal to the high purity, solar grade silicon metal. The hydro-

chlorination step (1) bears the greatest burden in terms of material processing since it produces the starting $SiHCl_3$ and recycles both the hydrogen and the $SiCl_4$ generated in the sequent reaction steps. Approximately 60 lb. of $SiCl_4$ are processed in this step in order to produce one lb. of SiH_4 down stream. Thus any improvements on the hydrochlorination reaction have a significant impact on the economics of the overall silane-to-silicon process. The goal of this research and development effort is to support the engineering development activities on the hydrochlorination process at Union Carbide with the aim to improve process efficiency and to reduce cost.

III. DISCUSSIONS

The reaction of $SiCl_4$ and $SiHCl_3$ with hydrogen gas at elevated temperatures to deposit silicon metal has been extensively studied. It forms the basis for the so-called Siemens Process for the production of high purity silicon metal used in the electronics industry. The reaction equilibria in a silicon-hydrogen-chlorine system are well-established[1,2]. Depending on the reaction conditions and on the hydrogen to chlorine ratios, one can operate a process so as to deposit silicon metal in a vapor phase deposition process. On the other hand, one can vary the reaction conditions to effect the reversed reaction to consume

silicon. The reaction conditions for the hydrochlorination of $SiCl_4$ and m.g. silicon metal,



$$3\ SiCl_4 + 2H_2 + Si \rightleftarrows 4\ SiHCl_3 \quad (1)$$

are so chosen as to maximize the formation of trichlorosilane. Interestingly, this reaction was first observed by O. Ruff and K. Albert[3] in 1905, who reported a reaction identical to the reversed reaction in Equation (1). The same reaction was studied by Union Carbide at their Tonowanda Laboratories in the late 1940[4] and it forms the basis of the closed-loop, silane-to-silicon process developed under the JPL Contract No. 954 334. The reaction in Equation (1) results a net volume contraction as $SiHCl_3$ is produced. As the law of thermodynamics predicts, higher reactor pressure produces a higher conversion to $SiHCl_3$. The experimental hydrogenation reactor at MIT is specifically designed to operate at these high pressures in order to optimize the reaction conditions.

A. <u>The Hydrochlorination Apparatus</u>

The apparatus for the hydrochlorination of $SiCl_4$ and m.g. silicon metal to $SiHCl_3$ is schematically shown in Figure I. The stainless steel pressure reactor was designed to operate at pressures up to 500 psig. The 500 psig pressure is also the proposed operating pressure for the hydrochlorination reactor in the Union Carbide EPSDU, silane-to-silicon process[4]. A

constant flow of hydrogen gas from a cylinder is metered through a fine needle valve. The hydrogen gas pressure is controlled by a pressure regulator which sets the gas pressure about 50 psig above the selected reactor pressure for the hydrogenation. The gas flowrate is measured by a mass flowmeter. The hydrogen gas is dispersed into a liquid column of $SiCl_4$ contained in a stainless steel cylinder. The $SiCl_4$ liquid is heated by circulating a heat transfer fluid from a constant temperature bath through the condenser jacket around the stainless steel cylinder. The molar ratio of the $H_2/SiCl_4$ feed stream can be conveniently selected by adjusting the $SiCl_4$ liquid temperature and by the applied hydrogen gas pressure. Since the vapor pressure of the $SiCl_4$ liquid is constant at a given temperature, the $H_2/SiCl_4$ feed ratio remains constant even though the flowrate of the hydrogen gas varies. The gaseous $H_2/SiCl_4$ mixturc is fed into the bottom of the one-inch inside diameter hydrochlorination reactor containing the Si mass bed. The reactor tube is made of Type 304 stainless steel 1-1/4 inches outside diameter by 30 inches long. The reactor is electrically heated. In addition to the main heater which controls the reactor temperature through a thermocouple from the temperature controller, there are four sectional heaters placed along the reactor tube. These sectional heaters can be individually adjusted so as to compensate for the different degree of heat loss along the hydrochlorination reactor especially at the end of the reactor tube. A stainless steel metal block is connected

to the $H_2/SiCl_4$ inlet at the bottom of the reactor as shown in Figure II. The stainless steel block raises the Si mass bed about six inches from the bottom of the reactor. The Si mass bed is now totally enclosed by the electric heaters. A uniform temperature profile along the reactor tube can be achieved by fine tuning the individual electric heaters. The stainless steel block also serves as a preheater for the incoming $H_2/SiCl_4$ gaseous mixture. The reactant gas is dispersed into the Si mass bed through a g r i d plate welded onto the top of the stainless steel block. The grid plate is a 5-orifice design as shown in Figure II. This design was selected from several variations by experimenting with a fluidized-bed of Si metal in a one-inch inside-diameter glass tubing. The quality of fluidization is judged visually. The 5-orifice grid appears to give the best results.

An inlet port is provided at the top of the hydrochlorination reactor. Fresh Si metal and copper catalyst can be pressure-charged into the reactor from a small stainless steel cylinder. In a continuous reaction, silicon metal is intermittently charged into the hydrochlorination reactor to maintain the Si mass bed at a constant level. A thermocouple well is placed inside the reactor extending from the top of the reactor tube to about one inch above the grid plate. The thermocouple from the temperature

controller is placed at about the mid-poind of the Si mass bed. The temperature profile of the Si mass bed is readily measured by moving the thermocouple up or down inside the thermocouple well. The reaction product mixture coming out the hydrochlorination reactor is condensed by the -65°C condenser assembly as schematically shown in Figure I. Cooling to the -65°C condenser is provided by circulating a coolant from a Dry-Ice reservoir through the condenser jacket. The condensed chlorosilane product mixture is collected in the 2-1/2 gallon stainless steel receiver. The liquid products can be withdrawn from the receiver through a needle valve. The unreacted hydrogen gas is vented into the fume hood after it is reduced to atmospheric pressure through a back pressure regulator. The back pressure regulator also controls the pressure inside the hydrochlorination apparatus. The reaction product mixture is analyzed by an in-line gas chromatograph as described in Section B in the following.

B. The In-Line Gas Chromatograph

An in-line gas chromatograph is connected directly to the outlet of the hydrochlorination reactor. This in-line arrangement provides instantaneous analysis of the gaseous reaction product mixture. A gaseous sample from the reactor is drawn into the sample loop through a needle valve and a filter arrangement as

shown in Figure I. All the connecting tubings are heat-traced so that the sample is maintained in a homogeneous vapor state. The sample in the sample loop is injected into the column by turning the G.C. sampling valve. The analytical column is 1/8 inch O.D. x 12 ft. packed with 5% SE-30 silicone gum stationary phase on 150 mesh Chromosorb W. A standard hot wire detector is used for the analysis. The G.C. spectrum is recorded and analyzed by the Hewlett-Packard Model 3380A Recorder/Integrator. The in-line arrangement eliminates the need for external sampling of the chlorosilane liquid mixture. About 1 - 2% of "heavies" was previously reported in the analysis of the chlorosilane liquid products. These heavies are absent in the in-line G.C. analysis. Thus, these heavies are most likely hydrolysates produced by the hydrolysis of the chlorosilanes in contact with air and moisture during the sampling procedure.

C. Reaction Kinetic Measurements

A series of experiments was carried out to measure the rate of the hydrochlorination reaction as a function of temperature, pressure and $H_2/SiCl_4$ feed ratio. The reaction rate was followed by measuring the rate of product formation as a function of varying residence times. The only major product in the hydrochlorination of $SiCl_4$ and m.g. silicon metal is $SiHCl_3$. The presence of a small amount of SiH_2Cl_2 is the only significant by-product. The reaction product composition

was analyzed by the in-line gas chromatograph. Duplicate analyses were made on each of the reaction rate measurements until two consecutive analyses agreed within ±2%. The residence time was varied by gradually increasing or decreasing the $H_2/SiCl_4$ feedrate. It is defined as the movement of the inlet gaseous mixture passing through an empty reactor tube with a volume equal to the volume of the 65 x 150 mesh Si mass bed. The volume of the Si mass bed is obtained by dividing the weight of the Si metal by its bulk density of 1.2. For example, if the feedrate of the $H_2/SiCl_4$ gaseous mixture under the reaction conditions is 100 c.c. per minute, the residence time is calculated to be 60 seconds with a 120g Si mass bed inside the hydrochlorination reactor. The residence time as defined is a hypothetical number which provides a convenient common denominator to simplify the treatment of experimental rate data. Parameters which influence the gaseous flow through the Si mass bed, such as particle size distribution (void space in the mass bed), volume contraction as $SiHCl_3$ is produced (Equation 1), bed expansion due to gas bubbles (fluidization mode), etc. are not included in the residence time measurements. These parameters were studied individually in separated experiments. In each of the reaction rate measurements, a mass balance was made to calculate the amount of Si metal consumed by the hydrochlorination

reaction. The weight of the remaining Si metal inside the reactor was used to calculate the residence time as defined above.

(1) Function of Temperature

A series of experiments was carried out to study the effect of temperature on the rate of the hydrochlorination reaction at reactor pressure of 500 psig and with a $H_2/SiCl_4$ feed ratio of 2.8. The reactor was initially charged about 200 g 65 x 150 mesh (210 x 105 microns) m.g. silicon metal. The reaction was run for a few hours until a steady state was reached. Then, reaction kinetic measurements were made. Table I summarizes the reaction kinetic data at 500°C. Data in Table I are also presented in Figure III by plotting the % $SiHCl_3$ conversion versus residence time. The small amount of SiH_2Cl_2 by-product is neglected. The same reaction was repeated at 450°C and 550°C. The results of these two experiments are summarized in Table II (450°C) and in Table III (550°C) respectively. Data in Table II and Table III are also plotted in the same graph in Figure III for the 500°C experiment. The reaction kinetic curves in Figure III are typical of an equilibrium reaction. Initially, the % conversion of $SiHCl_3$ increases rapidly with respect to residence times, the curves in Figure III level off at the equilibrium conversion of $SiHCl_3$. The hydrochlorination reaction rate is defined as the rate at which the conversion of $SiHCl_3$ is approaching its equilibrium value. The large effect of temperature on the reaction rate is clearly shown in Figure III. As

expected, the rate of reaction increases rapidly with rising reaction temperatures.

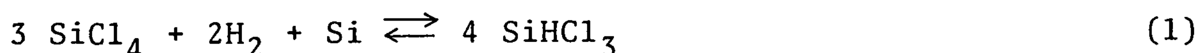
As presented in Figure III, the plots at 450°C and at 550°C show a smooth curve. The graph of these two temperatures represent single tests carried out for short periods of time within one day. On the other hand, the plot at 500°C represents a collection of separated experiments with a Si mass bed at various stages of conversion. The more noticeable scattering of data points in the 500°C plot represents a larger deviation of experimental errors when the reaction kinetic data from one experiment are measured in comparison with those of another experiment carried out under similar reaction conditions. Another series of experiments was carried out to study the effect of temperature on the hydrochlorination reaction rate at a lower reactor pressure of 300 psig and with a $H_2/SiCl_4$ feed ratio of 1.0. Results of these experiments are summarized in Table IV (550°C), Table V (500°C), Table VI (450°C) and Table VII (400°C). Data in these tables are also plotted in Figure IV. The graphs in Figure IV again show a large effect of reaction temperature on the reaction rate. Interestingly, at temperature as low as 400°C, the hydrochlorination of $SiCl_4$ and m.g. silicon metal proceeded at a respectable rate to produce 21% conversion of $SiHCl_3$ at 180 seconds residence time. Data in Figure III and Figure IV show that higher reaction temperatures not only produce a faster reaction, but also gave a higher $SiHCl_3$ conversion. The higher equilibrium conversion of $SiHCl_3$ at higher reaction temperatures is due to a positive free energy of

formation $(\Delta G)_f$ for the hydrochlorination reaction, which was observed in the earlier contract work carried out at Union Carbide. The present experimental results are similar to those reported previously[4]. The significance of the above reaction kinetic measurements is that the data were collected at reactor pressure of 500 psig which is also the proposed pressure for the hydrochlorination reactor in the Union Carbide EPSDU. Since a higher reaction temperature produces both a higher reaction rate and a higher $SiHCl_3$ conversion, the highest practical reaction temperature may be used to maximize reactor output.

(2) Function of $H_2/SiCl_4$ Feed Ratio

A series of experiments was carried out to study the effect of hydrogen and $SiCl_4$ concentrations on the reaction rate and on the product $SiHCl_3$ conversion. The concentration of the reactants is expressed in terms of the $H_2/SiCl_4$ molar ratios which can be easily controlled in the hydrochlorination experiments. The experiments were carried out at a reactor pressure 300 psig and with a $H_2/SiCl_4$ ratio of 2.8. The reaction temperature was varied at 500°C, 450°C and 400°C respectively. The results of these experiments are summarized in Table VIII (500°C), Table IX (450°C) and Table X (400°C). Data in these tables are also presented in Figure V by plotting the % $SiHCl_3$ conversion versus residence time. As data in Figure V show, the % $SiHCl_3$ conversion is significantly higher than those obtained at a lower $H_2/SiCl_4$ feed ratio of 1.0 (Figure IV). The effect of $H_2/SiCl_4$ feed ratio on the hydrochlorination reaction can be more clearly seen in

Figure VI by plotting one set of the kinetic data at 2.8 and 1.0 $H_2/SiCl_4$ ratio obtained under the same reaction conditions at 500°C, 300 psig. The higher conversion of $SiHCl_3$ at a higher $H_2/SiCl_4$ molar ratio is expected, since the formation of $SiHCl_3$,



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

consumes hydrogen. An increase of the hydrogen gas partial pressure drives the equilibrium reaction (1) to the right hand size to produce more $SiHCl_3$.

Although a higher $H_2/SiCl_4$ feed ratio gives a higher $SiHCl_3$ conversion, the production rate of $SiHCl_3$ in terms of lb./hr. for a given reactor size is reduced by the presence of an extra amount of hydrogen gas. On the other hand, a higher $SiHCl_3$ conversion reduces the size of the $SiCl_4$ recycle stream since more $SiCl_4$ is converted to product $SiHCl_3$. The optimum $H_2/SiCl_4$ feed ratio is at best a compromise between the output of $SiHCl_3$ for a given reactor size and the amount of $SiCl_4$ needed to be re-cycled from the subsequent distillation/separation step.

(3) Function of Pressure

The effect of reactor pressure on the hydrochlorination of $SiCl_4$ and m.g. silicon metal can be seen by the reaction kinetic data obtained at 500 psig (Figure III) in comparison with those obtained at 300 psig (Figure V). The effect can be more easily observed in Figure VII by plotting the two sets of data in the same graph. For example, Figure VII shows the effect of pressure on both the reaction rate and the $SiHCl_3$ conversion at 450°C and

with a $H_2/SiCl_4$ feed ratio of 2.8; but at different reactor pressures of 500 psig and 300 psig respectively. The effect of reactor pressure on the hydrochlorination reaction is most interesting. As shown in Figure VII, the rate of approaching the equilibrium conversion of $SiHCl_3$ is somewhat slower at 500 psig than that at 300 psig. For example, at residence time less than 120 seconds, the % $SiHCl_3$ conversion is higher at 300 psig than those obtained at 500 psig. This implies a higher reaction rate at a lower reactor pressure. However, at residence time longer than 120 seconds, the % conversion of $SiHCl_3$ becomes higher at 500 psig than those obtained at 300 psig. This is not unexpected, since the formation of $SiHCl_3$ results in a net volume contraction as shown in Equation (1). As the reaction approaches equilibrium at long residence times, the formation of product $SiHCl_3$ is thermodynamically more favorable at higher reactor pressures. On the other hand, the kinetic measurements at short residence time showed a slower reaction at higher pressure. This phenomenon is not fully understood at the present time.

Figure VIII shows similar results on the effect of reactor pressure. Two sets of reaction kinetic data obtained at reaction temperature of 500°C and with a $H_2/SiCl_4$ feed ratio of 2.8 are plotted in the same graph. The reaction kinetic curves in Figure VIII again show a slower reaction rate at the higher reactor pressure of 500 psig in comparison with those obtained at 300 psig. At long residence times, the conversion of $SiHCl_3$ becomes higher at 500 psig than that obtained at 300 psig. Although the hydrochlorination

reaction rate is somewhat slower at 500 psig than that obtained at 300 psig, the production rate in terms of pounds per hour is still much higher at higher reactor pressures. For example, in Figure VIII at 60 seconds residence time, the slower reaction rate at 500 psig gives 30% $SiHCl_3$ while the faster reaction at 300 psig gives 32% $SiHCl_3$. However, the throughput of a given reactor size is increased by 64% when the reactor pressure is raised from 300 psig to 500 psig. For example, a reactor produces 1,000 lb./hr. of $SiHCl_3$ at 300 psig will make about 1,540 lb./hr. of $SiHCl_3$ at 500 psig with the same 60 seconds residence time; taking into account for the slower reaction rate at the higher reactor pressure. In order to maximize reactor output, the highest practical reactor pressure is recommended for the operation of the hydrochlorination process.

D. Copper Catalyst Studies

The effect of added copper catalyst on the hydrochlorination reaction rate was studied. The catalytic activity of copper is measured in terms of reaction rate in comparison with the reaction kinetic data obtained in Section (C) without copper added.

(1) Cement Type Copper

A series of experiments was carried out to study the hydrochlorination of $SiCl_4$ and m.g. silicon metal in the presence of 5 wt% of a cement type copper supplied by Union Carbide. This cement type copper is a complex mixture of CuO, Cu_2O and Cu°. A mixture of 180g 65 x 150 mesh m.g. silicon metal and 9g (5 wt%) of cement cooper powder was thoroughly mixed and carefully charged

into the hydrochlorination reactor. The reactor was brought up to reaction conditions at 500 psig, 500°C and a $H_2/SiCl_4$ ratio of 2.8. The reaction rate was measured in the same manner as described in Section (C). An "induction period" of about 20 hours was noted, during which no catalytic activity was observed. This induction period is illustrated in Figure IX. In Figure IX, the reaction rate with 5% cement copper is presented as a function of reaction time (% conversion of the Si mass bed). The reaction rate obtained under the same conditions with no copper added is also plotted in the same graph (dotted line). At the start of the reaction (0% conversion), the hydrochlorination reaction rate is actually slower than those obtained without copper added. The slower reaction rate may be due to the presence of the inactive copper powder which occupies some space on the silicon metal surface. The % Si conversion is defined as the weight of Si consumed by the reaction divided by the weight of the silicon metal initially charged. It is directly related to the total reaction time to reflect the "age" of the Si mass bed. After 20 hours of reaction (about 25% Si conversion), the presence of the cement copper began to show some catalytic activities. At this point, the reaction rate with copper became faster than without copper added.

After the reactivity of the Cu/Si mass bed stabilized, a series of experiments was carried out to measure the rate of the hydrochlorination reaction as a function of temperature (450°C, 500°C), pressure (300, 500 psig) and $H_2/SiCl_4$ feed

ratio (1.0 and 2.8). Table XI summarizes the reaction kinetic data obtained with the cement copper/silicon mass at 500 psig, 500°C and a $H_2/SiCl_4$ feed ratio of 2.8. Data in Table XI are presented in Figure X by plotting the % $SiHCl_3$ conversion and the % SiH_2Cl_2 conversion versus residence time. Also plotted in the same graph are experimental rate data previously obtained from the same hydrochlorination reaction under similar conditions but with no copper added. The presence of copper significantly increases the reaction rate as shown in Figure X. Another series of experiments was repeated at a lower reaction temperature of 450°C. The reaction kinetic measurements are summarized in Table XII. The same data are plotted in Figure XI together with previously obtained results from the same reaction with no copper added. As the results in Figure XI shows, the hydrochlorination reaction rate in the presence of cement copper is approximately doubled in comparison with those obtained without copper. For example, in the presence of copper, 23% conversion of $SiHCl_3$ is observed at 30 seconds residence time (solid line). With no copper, the same 23% $SiHCl_3$ conversion is achievable at a residence time twice as long (60 seconds, dotted line in Figure XI).

The effect of copper on the reaction rate was also studied at a lower reaction pressure of 300 psig. Table XIII and Table XIV summarize the results of the reaction kinetic measurements at 500°C and at a different $H_2/SiCl_4$ feed ratio of 1.0 and 2.8 respectively. Data in Table XIII and Table XIV are also presented in Figure XII and Figure XIII, respectively, together with previous experimental

results obtained from the same reaction without copper. The results of the 300 psig experiments are very similar to those obtained at 500 psig. In the presence of copper, the reaction rate is increased by approximately 100% in comparison with those obtained under the same reaction conditions but with no copper added.

(2) Cuprous Chloride

A "reactive" copper compound was evaluated as catalyst for the hydrochlorination of $SiCl_4$ and m.g. silicon metal to $SiHCl_3$ Cuprous chloride, CuCl, is known to react with Si[5] at about 350°C in a displacement reaction,

$$4\ CuCl + Si \xrightarrow{\Delta} SiCl_4 + 4\ Cu \qquad (5)$$

Copper generated from Equation (5) is deposited onto the silicon metal surface. The copper atoms generated in this chemical reaction can diffuse into the silicon metal lattics to form what is generally known as Cu-Si alloys. These Cu-Si alloys have been reported to be the catalytic species for a variety of reactions between organic halides and silicon metal to produce organo-function silicon halides[6]

A series of experiments was carried out in the presence of 5 wt% CuCl in the same manner as in the case of the cement copper. A sample of cuprous chloride was ground and sieved through a 400 mesh screen (opening 38 microns). A mixture of 180g 65 x 150 mesh (210 x 105 microns) m.g. silicon metal and 9g of this CuCl powder was thoroughly mixed and carefully charged into the hydrochlorination reactor. The reactor was brought up to reaction conditions at 500 psig

and at 500°C. In contrast to the case with cement copper, there was no induction period observed with cuprous chloride. Full catalytic activity was noted soon after the hydrochlorination reactor was brought up to the reaction temperature. The absence of an induction period is shown by the plots in Figure XIV. Unlike cement copper, the CuCl/Si mass bed at the start of the experiment (0% Si conversion) showed significantly higher reactivity than that obtained without copper (dotted line). Furthermore, the reactivity of this Cu/Si mass bed remained constant with respect to reaction time. As Figure XIV shows the reaction rates at the start of the experiment (0% Si conversion) is the same as those obtained after 25% Si conversion. A series of experiments was carried out to measure the rate of reaction as a function of reaction temperature (400°, 450° and 500°C), reactor pressure (300, 500 psig) and $H_2/SiCl_4$ feed ratio (1.0 and 2.8). Table XV summarizes the reaction kinetic measurements obtained with the 5% CuCl/Si mass at 500 psig, 500°C and $H_2/SiCl_4$ feed ratio of 2.8. Data in Table XV are presented in Figure XV by plotting the $SiHCl_3$ and SiH_2Cl_2 conversions versus residence time. Also plotted in the same graph are experimental data previously obtained from the same hydrochlorination reaction under similar reaction conditions but with no copper added. The presence of copper approximately doubles the reaction rate in comparison with those obtained with no copper added. As in the case of the cement copper, the % conversion of SiH_2Cl_2 is also increased in the presence of copper. Similarly, Table XVI and Figure XVI summarize the reaction kinetic

data obtained under the same reaction conditions but at a lower reaction temperature of 450°C. At the lower reaction temperature, the presence of copper appears to show a more pronounced effect. For example, in Figure XVI, 28% $SiHCl_3$ conversion is obtained at 40 seconds residence time with 5% CuCl in comparison with the 108 seconds residence time required to achieve the same 28% $SiHCl_3$ conversion with no copper. The presence of copper has increased the reaction rate by a factor of about 2.7. The same hydrochlorination reaction in the presence of copper was repeated at a lower reactor pressure of 300 psig. Table XVII and Table XVIII summarize the reaction kinetic measurements obtained at 300 psig and with a $H_2/SiCl_4$ feed ratio of 1.0, but at a different reaction temperature of 500°C and 400°C respectively. Data in these two tables are also plotted in Figure XVII and in Figure XVIII, respectively, together with the previously obtained experimental data collected under similar reaction conditions but with no copper added. The kinetic data obtained at 300 psig is similar to those obtained at 500 psig. Interestingly, at reactor temperature as low as 400°C, a respectable 24% $SiHCl_3$ conversion is achievable at 180 seconds residence time in the presence of copper (see Figure XVIII).

(3) Effect of Copper Concentration on the Reaction Rate

The effect of copper concentration in the Si mass bed on the rate of the hydrochlorination reaction was studied. A mixture of 180g 65 x 150 mesh m.g. silicon metal and 3.6g (2 wt%) CuCl was prepared and charged into the reactor. The experiment was carried

out at 300 psig, 500°C and $H_2/SiCl_4$ feed ratio of 1.0. There was a shot induction period with the 2% CuCl as shown by the reaction kinetic measurements presented in Figure XIX. The reaction rate at the start of the reaction (0% Si conversion) was slightly slower than the reaction rate after 25% of the Si metal in the Cu/Si mass bed had been consumed. The reactivity of the Cu/Si mass bed improved slightly with reaction time. The spreading of copper over the silicon metal surface may be the cause. The nature of the active copper catalyst will be discussed later on in Section (4). Results of the reaction kinetic measurements with 2% CuCl are summarized in Table XIX. The performance of this 2% CuCl/Si mass bed is shown in Figure XX by plotting the % $SiHCl_3$ conversion versus residence time. Also plotted in the same graph are reaction rate data obtained from the same reaction with 5% CuCl added and from the same reaction with no copper added. As the results in Figure XX show, there is no difference between the reaction rates obtained from the 5% CuCl and the 2% CuCl experiment. Interestingly, the same level of reactivity is produced with the 5 wt% cement copper in the Si mass bed. After going through the induction period, the cement copper/Si mass gave the same reactivity as that of the CuCl/Si mass bed. This observation is illustrated in Figure XXI by plotting the reaction kinetic data obtained from the 5% cement copper experiment and from the 5% CuCl experiment in the same graph. As the results in Figure XXI show, there is essentially no difference between the reaction rates in the presence of these two copper compounds. The numbers in the

parenthesis are the % Si conversion to reflect the age of the silicon mass beds.

In summary, copper is an effective catalyst for the hydrochlorination of $SiCl_4$ and m.g. silicon metal to $SiHCl_3$. The reaction rate is increased by approximately 100% with as little as 2 wt% CuCl present in the Si mass bed. Other than a slightly slower initial reaction rate, the performance of the 2 wt% CuCl in the hydrochlorination reaction is essentially the same as the 5 wt% CuCl in the Si mass bed. In contrast, the 5 wt% cement copper experiment showed a long induction period. Before the cement copper is "activated" through this induction period, the reaction rate is actually slower than the reaction rate obtained with no copper added. In this respect, cuprous chloride is the preferred catalyst over cement copper. The lower level of 2 wt% CuCl catalyst for the hydrochlorination reaction is preferable from a process and from an economics point of view.

(4) Reaction Mechanism and the Role of Copper

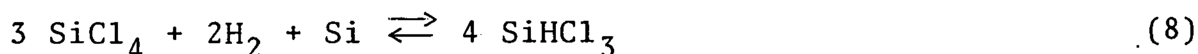
The reaction kinetic measurements as presented in Figure X through Figure XX show that, at long residence time, the % $SiHCl_3$ conversion in the presence of copper tends to level off at about the same position as those obtained from the same hydrochlorination reaction with no copper present. In other words, both kinetic curves, with and without copper, approach the same equilibrium conversion of $SiHCl_3$. In this respect, copper performes in the hydrochlorination as a true catalyst since it changes the reaction rate but not the equilibrium composition.

A plausible mechanism for the hydrochlorination of $SiCl_4$ and m.g. silicon to $SiHCl_3$ may be postulated as a first slow, rate-determining step on the hydrogen reduction of $SiCl_4$ to $SiHCl_3$ and HCl on the silicon metal surface (Equation 6). This is followed by a rapid reaction of the HCl with silicon metal to produce more $SiHCl_3$ (Equation 7). The overall reaction, 3 x (6) + (7), gives equation (8) for the hydrochlorination of $SiCl_4$ and m.g. silicon metal to $SiHCl_3$.

$$SiCl_4 + H_2 \underset{}{\overset{slow}{\rightleftharpoons}} SiHCl_3 + HCl \qquad (6)$$

$$3HCl + Si \overset{fast}{\rightleftharpoons} SiHCl_3 + H_2 \qquad (7)$$

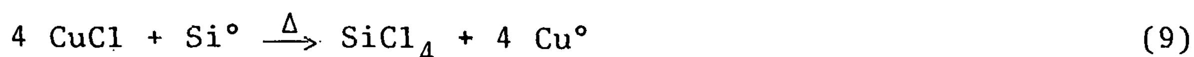
3 x (6) + (7)



$$3\ SiCl_4 + 2H_2 + Si \rightleftharpoons 4\ SiHCl_3 \qquad (8)$$

The copper catalyst studies with cement copper and cuprous chloride provide some experimental evidence of the mechanism of the hydrochlorination reaction as postulated above and on the nature of the copper catalyst. An induction period is observed when cement copper is used in the hydrochlorination reaction. This induction period is absent when cuprous chloride is used in the same reaction. As the hydrochlorination reaction proceeds, both cement copper and caprous chloride ultimately produce the same catalytic activities. Furthermore, 2% CuCl works equally well as the 5% CuCl present in the hydrochlorination reaction to produce the same reaction rates. Since the oxide-based cement copper is rapidly reduced by hydrogen

at 500°C to elemental copper, the induction period may be explained as the time required for this "free" copper to form the active catalytic species on the silicon metal surface. This also points to the fact that elemental copper (free copper) is not a catalyst in the hydrochlorination reaction. However, once the cement copper is activated through the induction period, it shows the same catalytic activity as observed with CuCl. These pieces of experimental evidence suggest that a common catalytic species is formed during the hydrochlorination reaction even though two different forms of copper compound are initially used. Since Cu-Si alloys are known to form on the silicon metal surface[6] when CuCl reacts with Si metal under the reaction conditions, the active catalytic species must be the copper-silicon alloys.



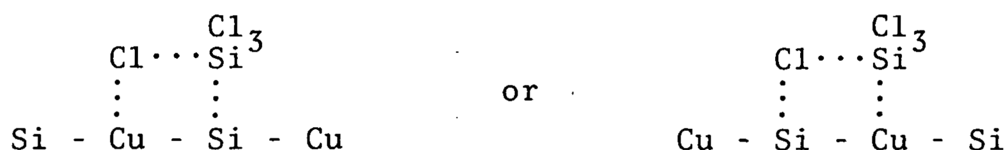
$$4\ CuCl + Si^\circ \xrightarrow{\Delta} SiCl_4 + 4\ Cu^\circ \qquad (9)$$

$$Cu^\circ + Si^\circ \longrightarrow Cu\text{-}Si\ \text{alloy} \qquad (10)$$

The energetic copper atoms produced in the chemical reaction (9) can diffuse into the silicon metal matrix to form Cu-Si bonds in the copper-silicon alloys. On the other hand, the oxide-based cement copper is first rapidly reduced by hydrogen at 500°C to elemental copper. The elemental copper does not thermally form these copper-silicon alloys at a significant rate under the low reactor temperature of 500°C. The copper powder must go through a chemical transformation (most likely to copper chloride) so that the Cu-Si alloys can be produced through a chemical reaction with

the Si on the solid surface. The induction period observed with cement copper is thus the time required for this chemical transformation to take place. On the other hand, cuprous chloride is a reactive chemical toward silicon metal. The Cu-Si alloys are rapidly formed on the silicon metal surface at temperatures well below 500°C. Thus, no induction period is expected with CuCl.

The mechanism of the hydrochlorination of $SiCl_4$ may be visualized as a first step chemisorption of $SiCl_4$ at the Cu-Si sites, viz.,



followed by the reduction of the activated Si---Cl, Si---Si and Cu---Cl linkages by hydrogen to form $SiHCl_3$ and HCl. This is the slow, rate-determining step occuring at the silicon metal surface. The intermediate HCl rapidly reacts with Si at the Cu-Si catalytic site since HCl gas is known to react with silicon metal at a much lower temperature of 300-350°C[3,7]. As Si is consumed to form $SiHCl_3$, the vacated site is filled by migration of Si atoms from the under-layers to re-generate the active Cu-Si species to complete the catalytic cycle of copper. The mechanism is very similar to the reaction mechanism of the well-known Direct Reaction between methyl chloride and silicon metal to produce methylchlorosilanes[5]. The presence of these Cu-Si alloys is essential for the CH_3Cl + Si reaction[6].

The catalytic activity of copper may be interpreted as due to the crystal defects caused by the presence of copper atoms in the silicon crystal lattics. Further experimental evidence on this postulation is provided in the Impurities Studies which is discussed later on in Section (F). Since the active copper catalyst is the copper-silicon alloys containing Cu-Si bonds, loose copper particles or highly concentrated copper deposits on the silicon metal surface do not provide an effective catalyst. In practice, one needs to add more copper to the Si mass bed than that is theoretically needed to generate these active Cu-Si sites. Thus, the absolute amount of copper present in the Si mass bed is not the factor in determining the catalytic activity of the Cu/Si mass bed. The total number of these active Cu-Si sites is the important parameter for the observed catalytic activities. As long as there are sufficient amounts of copper present in the Si mass bed to cover the silicon metal surfaces with these Cu-Si sites, the ultimate reactivity of the Cu/Si mass bed is the same regardless of the total amount of copper initially charged. This is shown by the experiment with 2% CuCl which produces the same catalytic activity as the 5% CuCl in the Si mass bed (see Figure XX). Thus, the method and the procedure for preparing the Cu/Si mass are equally important parameters. For example, 2 wt% CuCl in the Si mass produces a more reactive Cu/Si mass bed than that of the 5 wt% cement copper. This is because cuprous chloride forms the active Cu-Si species more efficiently than cement copper.

E. Silicon Particle Size Distribution

The effect of silicon particle size distribution on the hydrochlorination reaction rate was studied as a function of reactor pressure, reaction temperature and $H_2/SiCl_4$ molar ratio. The 65 x 150 mesh m.g. silicon metal was used as the standard in previous experiments. Two particle size distributions of m.g. silicon metal, 150 x 400 mesh and 32 x 65 mesh, were evaluated in the hydrochlorination reaction. Table XX summarizes the physical properties of these three particle size distributions of silicon metal, such as the mean particle size, surface area, bulk density and % void space.

A series of experiments was carried out with 180g 32 x 65 mesh m.g. silicon at reactor pressure of 500 psig, reaction temperature of 500°C and $H_2/SiCl_4$ feed ratio of 2.8. Reaction kinetic data were collected in the same manner as previous experiments by measuring the rate of $SiHCl_3$ formation as a function of residence time. The results of these measurements are summarized in Table XXI. Another series of experiments was carried out under the same reaction conditions with a much finer 150 x 400 mesh silicon particle size distribution. Results of this series of experiments are given in Table XXII. Data in Table XXI and in Table XXII are presented in Figure XXII by plotting the $SiHCl_3$ conversion versus residence time. Also plotted in the same graph are reaction rate data previously obtained from the standard 65 x 150 mesh silicon under the same reaction conditions. As the results in Figure XXII show, the different particle size

distributions of silicon metal have essentially no effect on the rate of the hydrochlorination reaction. The scattering of data points are within the experimental error. Thus, the hydrochlorination reaction rates remain constant within the silicon particle size distribution range of 32 x 400 mesh. Similar results were obtained when the reaction was carried out at a lower reactor pressure of 300 psig with the 150 x 400 mesh and the 32 x 65 mesh silicon metal. Results of these two experiments are given in Table XXIII and in Table XXIV respectively. The reaction rate data in these two tables are also presented in Figure XXIII by plotting the % $SiHCl_3$ conversion versus residence time. As the results in Figure XXIII show, there is essentially no difference in the reaction rate between the 150 x 400 and the 32 x 65 mesh silicon metal. The constant reaction rate with respect to Si particle size also implies that the hydrochlorination reaction of $SiCl_4$ and Si is also independent of the total solid surface area. For the same weight of the silicon mass bed, the 150 x 400 mesh particle size distribution has about five times the total surface area as the much coarser 32 x 65 mesh silicon. Despite the large difference in the total solid surface area, the reaction rate remains about the same. The results of these experiments show that the chemical reaction occurring on the surface of the silicon metal is the rate-determining step. Mass transfer via diffusion of reactants and products is not rate-limiting. This observation is in agreement with the postulated reaction mechanism as discussed in Section D (4) above. The reduction of the

chemically absorbed $SiCl_4$ with hydrogen on the silicon metal surface is the rate-determining step.

The constant reaction rate with respect to silicon particle size distribution is advantageous from a process point of view. It provides a broader operating latitude for the hydrochlorination process. For example, one can conveniently increase the output of $SiHCl_3$ by operating the hydrochlorination reactor at a higher reaction temperature to give a higher reaction rate. The increase in linear gas velocity due to the higher $H_2/SiCl_4$ feedrate can be compensated for by simply increasing the silicon particle size distribution. Since the hydrochlorination reaction rate is independent of the Si particle size, the % $SiHCl_3$ conversion remains the same.

F. <u>Effect of Impurities in m.g. Silicon Metal</u>

The metallurgical grade (m.g.) silicon metal contains about 98.5% Si. The major impurities in the m.g. silicon metal are iron (0.5 - 0.9%) and aluminum (0.3 - 0.6%). These two elements account for the bulk (80 - 90%) of the total impurities in the m.g. silicon metal. Other metallic elements are also present but in a much smaller amount, viz., Manganese (0.06%), Calcium (0.05%), Copper (0.01%), Nickel (0.01%), Chromium (0.01%) and Titanium (0.01%). To study the effect of each of these metallic impurities on the hydrochlorination reaction is beyond the scope of the present experimental effort. Rather, the overall effect of these impurities on the reaction is studied from the view point of operating the hydrochlorination process. A convenient method of studying the

overall effect of these impurities is to measure the reaction rate with the m.g. silicon metal in comparison with those obtained with a high purity, electronic grade silicon metal. The electronic grade silicon metal contains no impurities from the chemical reaction point of view, the common metallic impurities in the electronic grade silicon metal having been reduced to less than one part per billion.

A sample of electronic grade, polycrystalline silicon metal was ground and sieved to a particle size distribution of 32 x 400 mesh (500 x 37 microns). A series of experiments was carried out with 180g of this high purity Si at a reactor pressure of 500 psig, a reaction temperature of 500°C and a $H_2/SiCl_4$ feed ratio of 2.8. The results of this experiment are summarized in Table XXV. Data in Table XXV are present in Figure XXIV by plotting the % $SiHCl_3$ conversion versus residence time. Also plotted in the same graph are reaction kinetic data obtained with m.g. silicon metal under the same reaction conditions. The shaded curve in Figure XXIV represents the combined results obtained from the same reaction carried out with a 32 x 65 mesh, a 65 x 150 mesh and a 150 x 400 mesh m.g. Si metal mass bed. As the results in Figure XXIV show, the reaction rate is about one order of magnitude slower with the electronic grade Si metal in comparison with those obtained from the impure, 98.5% m.g. Si metal. The presence of these metallic impurities in m.g. silicon metal greatly increases the rate of the hydrochlorination of $SiCl_4$ and hydrogen.

The effect of added copper catalyst was also studied. The electronic grade Si mass bed was taken out of the hydrochlorination reactor and mixed with 9g (5 wt%) of the -400 mesh cuprous chloride powder used in the copper catalyst studies (Section D). The mixture was carefully charged back into the reactor tube. Then, the experiment was repeated under the same reaction conditions. Results of this experiment are summarized in Table XXVI. The reaction kinetic data in Table XXVI are also presented in Figure XXV by plotting the % $SiHCl_3$ conversion versus residence time. Also plotted in the same graph are the reaction rate data obtained in Section (D) with a 5% CuCl/m.g. silicon mass bed under the same reaction conditions. Interestingly, results in Figure XXV show that the reaction rates obtained from the 5% CuCl + electronic grade Si experiment are essentially the same as those obtained from the 5% CuCl + m.g. Si experiment. These experimental results appear to show that the impurities in the m.g. silicon metal function like a catalyst. Evidently, the hydrochlorination reaction rate is very much dependent on the composition of the silicon metal surface. With an orderly oriented crystal lattics such as those on the surface of the electronic grade, polycrystalline silicon metal, the reaction rate is much slower by about an order of magnitude. The presence of copper and other metallic elements on the silicon metal surface greatly increases the rate of the hydrochlorination reaction. Thus, the crystal defects caused by the presence of copper or other metallic elements appear to be the mechanism for the observed catalytic

activities. However, results of the Copper Catalyst Studies in Section (D) show that the presence of copper on the m.g. silicon metal surface increases the hydrochlorination reaction rate by another factor of two. In this respect, copper appears to be a more effective catalyst than these metallic impurities in m.g. silicon metal. Experimental evidences are lacking at the present time to provide a plausible mechanism to account for the differences. The presence of these metallic impurities in m.g. silicon metal do not appear to produce harmful effects. In fact, they are beneficial to the hydrochlorination reaction. Also, the application of a copper catalyst provides a convenient means to recycle off-specification solar grade silicon metal in the hydrochlorination reactor.

G. Mass Life Studies

Experiments on the hydrochlorination of $SiCl_4$ and m.g. silicon metal to $SiHCl_3$ were carried out with the object of studying the life of the silicon mass bed. In practice, the hydrochlorination process must be able to substain sufficiently long period of operation before it has to be shut down for service. Thus, the longevity of the silicon mass bed inside the hydrochlorination reactor is an important factor in operating the hydrochlorination process efficiently and economically. In a continuous operation, m.g. silicon metal was added to the reactor to replenish the Si consumed by the hydrochlorination reaction. In other gas-solid reactions, deterioration of the solid mass bed can occur after the

process has been operated for a certain period of time. The deterioration of the mass bed is largely due to accumulation of the impurities in the starting material and the non-volatile by-products produced by the chemical reactions. The presence of these undesirable materials can foul the reactive solid surface. As a result, the activity of the solid mass bed diminishes. Eventhough the impurities may be totally inert to the chemical reactions, their physical presence takes up space inside the reactor and indirectly reduce the reactor output. Thus, the ability of the moving gaseous stream to remove these impurities as elutriated fines out of the reactor is another important factor to consider. The purpose of the Mass Life Studies is to carry out the hydrochlorination reaction for long periods of time in order to observe the effect, if any, on the reaction rate. The prolonged reaction also provides sufficient reaction product to carry out a material balance on the hydrochlorination process. Analysis of the fine solids elutriated from the silicon mass bed can provide useful information on how the impurities are distributed inside the hydrochlorination reactor.

The hydrochlorination of $SiCl_4$ and m.g. silicon metal to $SiHCl_3$ is a clean reaction from a process point of view. First of all, the reaction itself does not produce any non-volatile by-products. The reactants consist of silicon, chlorine and hydrogen. Other than silicon metal itself, there are no solid by-products produced from the hydrochlorination reaction. $SiCl_4$ and hydrogen are purified through the recycle stream. Therefore, the

only significant source of impurities is the m.g. silicon metal itself. Fortunately, the bulk of the impurities in m.g. silicon metal are iron and aluminum. In the chlorine-rich reaction environment, iron and aluminum form volatile $FeCl_3$ (b.p. 315°C) and $AlCl_3$ (b.p. 183°C) which are readily removed from the reactor with the gaseous product stream.

(1) Effect of Prolonged Reaction on the Rate of the Hydrochlorination Reaction

A prolonged reaction of $SiCl_4$ and m.g. silicon metal in the presence of hydrogen was carried out at a reactor pressure of 300 psig, a reaction temperature of 500°C and a $H_2/SiCl_4$ feed ratio of 2.0. The experiment was run on a day-to-day basis. About 8 to 10 hours of reaction time were accumulated for each day of operation. A charging port at the top of the hydrochlorination reactor allowed a weighed sample of m.g. silicon metal to be intermittently charged into the reactor to replenish the Si consumed. Two hundred grams of the 32 x 400 mesh m.g. silicon metal was initially charged into the reactor. The reactor was brought up to the reaction conditions in the usual manner. The reaction rate was continuously monitored by analyzing the composition of the reaction product mixture with the in-line g.c. arrangement at regular intervals of 2 to 4 hours. The chlorosilane liquid products collected in the receiver was taken out and weighed at the end of each day of operation. The yields of $SiHCl_3$ and SiH_2Cl_2 in the reaction product mixture were measured and recorded. The total amounts of SiH_2Cl_2 and $SiHCl_3$ produced throughout the

prolonged experiment were used to carry out a material balance for silicon in Section (2).

The prolonged experiment was terminated after a total of 238 hours of reaction. Results of the reaction kinetic measurements are graphically presented in Figure XXVI by plotting the % $SiHCl_3$ conversion versus residence time. Each data point in Figure XXVI represents approximately the average of eight hours of reaction. These data points fall within a range of residence time of 25 to 45 seconds. The variable residence time is a result of the changing silicon mass bed height. As Si is consumed by the hydrochlorination reaction, the residence time is shifted to a lower number. It moves back to a higher number when fresh silicon metal is added into the reactor. As fresh m.g. Si is added from time to time during the course of the mass life studies, the data point in Figure XXVI move back and forth between 25 and 45 seconds of residence times. Although these data points show some scattering along the kinetic curve, the reaction rates are essentially constant within the range of experimental error throughout the 238 hours of reaction. Table XXVII summarizes the results of some selected data points shown in Figure XXVI. These selected data points have residence times which coincide with one another at about 32 seconds. As the results in Table XXVII show, the hydrochlorination reaction rate as measured by the % $SiHCl_3$ conversions at 32 seconds residence time remains constant throughout the 238 hours of reaction. Based on these reaction rate measurements, the silicon mass bed appears to have a long mass life. This is an

important factor since it shows that the hydrochlorination process can be operated continuously for a long period of time without interruptions.

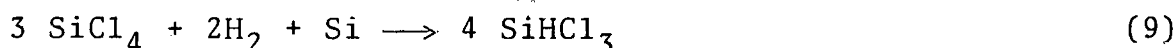
The same series of experiments was repeated with a copper catalyst added to the silicon mass bed. A mixture of 200g 32 x 400 mesh m.g. silicon metal and 10g (5 wt%) of the -400 mesh CuCl powder was prepared and charged into the hydrochlorination reactor. The reaction was carried out under the same conditions as the above experiment with no copper added at 300 psig, 500°C and $H_2/SiCl_4$ ratio of 2.0. As Si is consumed by the hydrochlorination reaction, a weighed sample of the 32 x 400 mesh silicon containing 5% CuCl catalyst is intermittently added to the reactor. The reaction rate is continuously monitored at 2 to 4 hour intervals by analyzing the composition of the reaction product mixture with the in-line gas chromatograph. After 90 hours of reaction, the experiment in the presence of copper was terminated. Results of the reaction kinetic measurements are presented in the same graph in Figure XXVI for the prolonged experiment without copper. As the results in Figure XXVI show, the reaction rate in the presence of copper remains essentially constant throughout the 90 hours of reaction. The scattering of data points on the kinetic curve is within the experimental error. As expected, the presence of copper catalyst approximately doubles the reaction rate in comparison with those obtained without copper (Figure XXVI).

There is other physical evidence which also points to the longevity of the silicon mass bed in the hydrochlorination reaction.

The spent Si mass bed was taken out of the reactor for examination after the experiments on the Mass Life Studies. Examination of the spent Si mass bed showed no evidence of aggregates or agglomeration of the silicon particles. The spent Si mass after 238 hours of reaction was completely free-flowing. Analysis of the elutriated fines showed a high concentration of metallic impurities in comparison with the starting m.g. silicon metal. Thus, the solid impurities are, at least, partially removed from the silicon mass bed out of the hydrochlorination reactor as elutriated fines. The results of these analyses are discussed in Section (3).

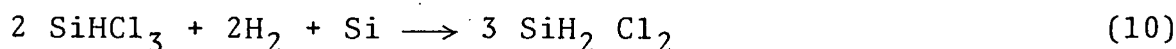
(2) Material Balance for Silicon

A material balance on silicon was made for the hydrochlorination of $SiCl_4$ and m.g. silicon metal to $SiHCl_3$,



$$3\ SiCl_4 + 2H_2 + Si \longrightarrow 4\ SiHCl_3 \qquad (9)$$

A total of 46,659g (103 lb.) of chlorosilane product crude was collecte during the course of the 238 hours of reaction in the prolonged experiment in Section (1). Analyses of the chlorosilane product mixture by gas-liquid partition chromatography showed the presence of 69g SiH_2Cl_2 and 7,944g (17.5 lb.) of $SiHCl_3$. The silicon consumption from these two chlorosilane products was calculated according to the above equation (9) for $SiHCl_3$ and equation (10) below for SiH_2Cl_2,



$$2\ SiHCl_3 + 2H_2 + Si \longrightarrow 3\ SiH_2\ Cl_2 \qquad (10)$$

The total Si equivalent from 69g of SiH_2Cl_2 and 7,944g of $SiHCl_3$ products was calculated to give a total of 417.6g Si metal consumed. The actual amount of Si metal consumption can be readily measured from the weight of the spent Si mass bed. A total of 570g m.g. silicon metal was charged into the reactor during the 238 hours of reaction. At the end of the experiments, 110.2g of unreacted Si metal was recovered. Thus, 570-110.2 = 459.8g m.g. silicon metal was consumed by the hydrochlorination reaction. Since the m.g. silicon metal is only 98.5% pure, the actual Si content was 459.8 x 0.985 = 452.9g. The material balance on Si is calculated to give,

$$\frac{417.6}{452.9} \times 100 = 92.2\%$$

The agreement is quite good. These results confirm the stoichiometry of the hydrochlorination reaction as written in Equation (9). As observed in previous experiments, the Si content calculated from the chlorosilane products was generally lower than the value obtained from the difference between the spent Si mass bed and the total silicon metal charged. This may be explained by the fact that some volatile SiH_2Cl_2 (b.p. 8°C) and $SiHCl_3$ (b.p. 31°C) are lost by evaporation during handling and storage.

(3) Distribution of Impurities in the Elutriated Fines

Sample of the fine solids elutriated from the silicon mass bed was collected and analyzed. This sample was taken from the prolonged experiment with no copper catalyst added. Since the linear gas velocity inside the laboratory scale reactor is slow,

the elutriated solids are extremely fine. These finely divided solids tend to spread out and coat the inside walls of the hydrochlorination apparatus. Thus, it was not possible to make a quantitative measurement on the total weight of the fine solids elutriated out of the silicon mass bed. Results of the analyses on the elutriated fines are summarized in the following:

Element	% in Elutriated Fines	% in M.G. Silicon
Iron	8.02	0.7
Aluminum	0.82	0.45
Calcium	1.19	0.05
Manganese	0.71	0.06
Nickel	0.15	0.01
Chromium	0.16	0.01
Chlorine	7.49	
Silicon (balance)	81.46	98.7

The metallic impurities in a typical m.g. silicon metal is shown in the last column. Results of these analyses show that the impurities in the m.g. silicon are concentrated by a factor of 10 or more in fine solids elutriated from the silicon metal mass bed. Aluminum is an exception since it is present at a much lower concentration in comparison with iron. This may be explained by the high volatility of $AlCl_3$ which can be removed along with the liquid chlorosilane crude. Deposition of the white $AlCl_3$ solid at the condenser and in the liquid chlorosilane crude has been observed in previous experiments. The presence of a large amount of chlorine in the elutriated fines indicated that some of the metallic elements are in the form of metal chlorides. However, the

amount of chlorine in the fines is not sufficient to account for all the metallic elements to exist in the form of metal chlorides. For example, if all the iron in the elutriated fines exists as $FeCl_3$, the chlorine contents would be in excess of 11%. As the above analytical results indicate, only 7.49% Cl are present in the fines. These interesting results suggest that some of these metallic impurities exist in an elemental state, or in the form of silicides. Although a quantitative account for the removal of these metallic impurities from the silicon mass bed is not achievable, the elemental analyses show that the impurities are, at least, partially removed from the hydrochlorination reactor.

H. Corrosion Studies

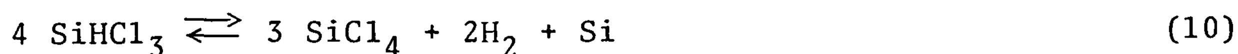
At elevated temperatures, HCl is produced in variable amounts in a reaction system containing chlorosilane and hydrogen gas. The highly corrosive effect of HCl gas on metals and alloys at high temperatures is well-known. Conventional metals and alloys offer little or no resistence to high concentrations of HCl gas at temperatures much above 450°C[8]. Under these conditions, a metal chloride film is formed on the metal surface. The covalent nature of metal chlorides exhibit a much higher vapor pressure than those of their oxide counterparts. At elevated temperatures, this metal chloride film begins to evaporate off. Corrosion becomes a serious problem as the material of construction of the reactor is constantly removed from the reactor wall as metal chlorides. In the chlorine-rich hydrochlorination reaction environment, the proposed operating temperature of 500°C poses a rather obvious potential threat to the

hydrochlorination reactor constructed with conventional metal alloys. This was a major concern in the engineering design of the hydrochlorination reactor, since high corrosion rates were reported in the earlier corrosion tests by Union Carbide[4].

Contradiction to this potential corrosion effect was first noted when the stainless steel reactor was cut up for examination. A dense coating appeared to cover the inside reactor wall which has been exposed to the hydrochlorination reaction environment. This dense coating is very similar to the epxitaxial silicon layers produced by a vapor phase deposition process. Upon exposure to air and moisture in the atmosphere, this dense coating was rapidly eroded to develop creeps and cracks. Eventually, it flaked off from the reactor wall. A sample of the loose flakes was analyzed to give the following results.

Element	% in Loose Flakes	% in typc 304 Stainless Steel
Nickel	6.61	8 to 11
Chromium	8.39	18 to 20
Iron	39.47	72 to 67
Silicon	17.83	Trace

The results of this analysis provide the evidence that a silicide film is formed on the reactor wall. The ratio of Ni:Cr:Fe in the silicide film is about the same as those in the Type 304 stainless steel. Evidently, silicon from the reversable hydrochlorination reaction,



$$4\ SiHCl_3 \rightleftharpoons 3\ SiCl_4 + 2H_2 + Si \qquad (10)$$

penetrates the reactor wall to form the observed silicide film. The concept of a metal chloride film on the reactor wall surface does not appear to operate in the hydrochlorination reaction environment. The presence of Si in the austenitic (non-magnetic) Type 304 stainless steel alters the structure and composition of the metal alloy. As a result, the loosened silicide film becomes magnetic. The presence of such a metal silicide protective film on the reactor wall opens up a new dimension on the subject of corrosion of the hydrochlorination reactor. The above observations show the following important facts.

(i) A metal silicide film is formed on the reactor wall instead of a metal chloride film.

(ii) This silicide film is reactive toward air and moisture.

(iii) Secondary corrosion rapidly destroys the protective silicide film when the reactor wall is exposed to the atmosphere.

A further corrosion study was made on a high nickel-chromium alloy, Incoloy 800H. It is the material of construction selected by Union Carbide for the hydrochlorination reactor EPSDU. A piece of the Incoloy 800H tubing, 1 inch O.D. x 1/16 inch wall, was supplied by Union Carbide for the corrosion studies. A test sample strip was cut from the pieces of Incoloy 800H tubing to fit inside the hydrochlorination reactor as schematically shown in Figure XXVII. The rings at the top and bottom of the middle strip are purposely

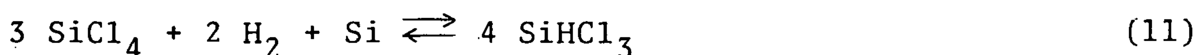
constructed so as to hold the sample at the side wall of the reactor tube. The corrosion test was carried out concurrently with the prolonged experiment in Section (G) at a reactor pressure of 300 psig, a reaction temperature of 500°C and a $H_2/SiCl_4$ ratio of 2.0. The test sample was weighed (53.195g) at the start of the experiment. After 238 hours of reaction, the sample was taken out and re-weighed: 53.520g. Thus, there was a weight gain of 53.520 - 53.195 = 0.325g. A dense coating appeared on the surface of the Incoloy 800 test sample. This coating had a physical appearance very similar to that obtained from the vapor phase deposition of Si with $SiHCl_3$ and H_2 at high temperatures. The test sample was measured to give a total surface area of 120 cm^2. Assuming the deposited material is Si and the coating is uniformly distributed, the 0.325g represents a weight gain of 0.00271 g/cm^2 or a silicon metal film of about 11.6 microns (micrometers) thick. The fact that there was no weight loss from the test sample indicates no significant amount of corrosion on the Incoloy 800H metal alloy.

After the Incoloy 800H test sample was re-weighed, it was immediately placed inside a Dry Box under an atmosphere of dry nitrogen. The middle strip (see Figure XXVII) was cut up with a pair of pliers. Pieces of the sample material were placed in glass ampoules. The glass ampoules then were sealed under nitrogen to prevent atmospheric corrosion of the test material. To study the effect of atmospheric corrosion on the silicide coating, the bottom ring (see Figure XXVII) was weighed (12.4025g). It was purposely exposed to air and moisture for a few days. As previously observed,

the dense silicide coating on the Incoloy 800H test sample readily developed creeps and cracks. Pieces of the coating flaked off from the metal surface. The dense surface coating was rapidly destroyed by atmospheric corrosion. After atmospheric corrosion had taken its effect, the loose scale was scraped off from the test sample with a spatula. The ring was cleaned, dried and re-weighed (12.1446g). Thus, there was a weight loss of 12.4026 - 12.1445 = 0.2581g. The bottom ring was measured to give a total surface area of 27 cm^2. The weight difference represents a weight loss of 0.00956 g/cm^2 in comparison with a weight gain of 0.00271 g/cm^2 before atmospheric corrosion had taken place. If one deducts the weight of silicon initially deposited on the test sample, there is still a net weight loss of 0.00956 - 0.00271 = 0.00685 g/cm^2. In other words, some base metal from the Incoloy 800H test sample was also taken off along with the loosened scale. Taking the density of Incoloy 800H as 8.0 g/c.c., about 8.6 microns of the base metal were removed from the metal surface with the silicon coating. These measurements provide further evidence that the silicon deposited from the hydrochlorination reaction penetrates the Incoloy 800H base metal to form a silicide protective film of approximately 20 microns thick. This silicide film appears to be stable inside the reactor under the hydrochlorination reaction environment. The 238 hours of reaction time were accumulated from 27 separated individual experiments. In other words, the Incoloy 800H test sample inside the reactor had gone through 27 start-up and 27 shut-down thermal cycles. There

is no evidence that this protective film has broken off from the base metal during the corrosion test. Had the silicide film been broken loose from the 800H test sample, a significant weight loss would have been noted. Furthermore, examination of the spent Si mass bed after the experiment showed no loose flakes of the silicide coating present in the Si metal powder. These experimental results show that a stable silicide film is formed at the reactor wall. The presence of such a silicide film can indeed protect the metal reactor from the hydrochlorination reaction environment.

Corrosion, or the lack of it, is largely determined by all the plausible chemical reactions reaching a state of equilibrium at the reactor wall. The most thermodynamically stable reaction or reactions will determine what is at the interface between the reactor wall and the hydrochlorination reaction environment. The deposition of Si can be readily explained by the reversible hydrochlorination reaction,



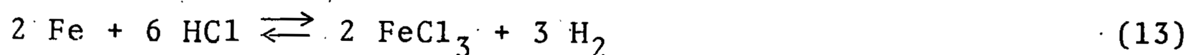
$$3\ SiCl_4 + 2\ H_2 + Si \rightleftarrows 4\ SiHCl_3 \qquad (11)$$

$$\text{Equilibrium Constant, } K = \frac{(SiHCl_3)^4}{(SiCl_4)^3 (H_2)^2}$$

The activity of Si metal is taken as unity. At the start of the reaction, the activity (Concentration) of Si is zero at the reactor wall. As the hydrochlorination proceeds, Si is deposited onto the metal surface until an equilibrium composition is reached. The Si atoms generated from the chemical

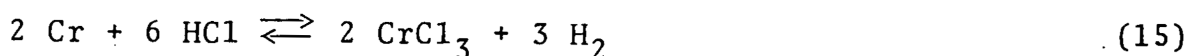
reaction can diffuse into the metallic matrix to form the silicide protective film. The actual surface conditions, at any time, depend on the system conditions, the equilibria and the kinetics of the reactions. With many elements present, there are many equilibria and complex reaction kinetics to be considered. The steady state composition of the silicide protective film depends on where the equilibrium of the hydrochlorination reaction lies and on other plausible reactions occuring at the interface. For example, HCl is known to be present in the silicon chloride/hydrogen system at elevated temperatures. It can react with silicon and the metallic elements at the reactor wall.

$$Si + 3\ HCl \rightleftarrows SiHCl_3 + H_2 \qquad (12)$$



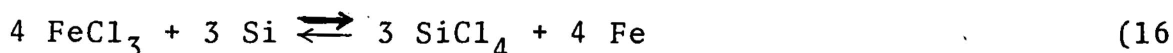
$$2\ Fe + 6\ HCl \rightleftarrows 2\ FeCl_3 + 3\ H_2 \qquad (13)$$

$$Ni + 2\ HCl \rightleftarrows NiCl_2 + H_2 \qquad (14)$$

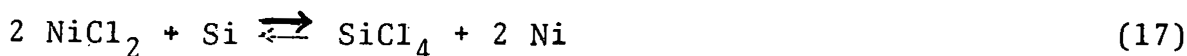


$$2\ Cr + 6\ HCl \rightleftarrows 2\ CrCl_3 + 3\ H_2 \qquad (15)$$

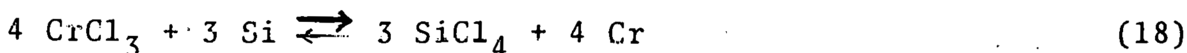
Metal chlorides also are known to react with silicon metal,[9]



$$4\ FeCl_3 + 3\ Si \rightleftarrows 3\ SiCl_4 + 4\ Fe \qquad (16$$



$$2\ NiCl_2 + Si \rightleftarrows SiCl_4 + 2\ Ni \qquad (17)$$



$$4\ CrCl_3 + 3\ Si \rightleftarrows 3\ SiCl_4 + 4\ Cr \qquad (18)$$

Since Si is more reactive toward HCl, silicon in the silicide film is preferentially reacted in the presence of HCl. As the activity of Si on the silicide film is lowered, silicon is re-deposited from

the reversed hydrochlorination reaction (11). This is a plausible mechanism from which the metal reactor wall is protected from the highly corrosive HCl gas at elevated temperatures. Although present at much lower concentrations, metal chlorides, such as $FeCl_3$, $NiCl_2$ and $CrCl_3$ can exist at the interface. The vapor pressure of these metal chlorides provides a driving force to remove these metallic elements from the reactor wall. On the other hand, the thermodynamically favored reactions (16), (17) and (18) provide the opposite driving force to keep these metallic elements on the reactor surface[9]. The high vapor pressure of titanium tetrachloride (b.p. 136°C) is the basis of an unstable Ti/Si silicide film since titanium in the silicide film constantly evaporates off as $TiCl_4$. Thus, titanium metal is not suitable for the material of construction for the hydrochlorination reactor as previously reported by Union Carbidc[4]. On the other hand, nickel and chromium produce the least volatile $NiCl_2$ and $CrCl_3$ among the chlorides of the conventional metals. Thus, silicides containing nickel and chromium form a stable protective film at the reactor wall as shown by the corrosion test for Incoloy 800H (40% Ni, 30% Cr, 30% Fe). Thus, these preliminary corrosion data show that Incoloy 800H is a good choice as the material of construction for the hydrochlorination reactor.

In conclusion, the corrosion test for Incoloy 800H produced evidence of a stable silicide protective film formed at the reactor wall. The extent of corrosion of the metal reactor by the hydrochlorination reaction environment was insignificant. However, care

should be taken to prevent atmospheric corrosion when the reactor is shut down for service or repair. The silicide procective film is readily destroyed by air and moisture. The serious corrosion problems as previously reported by Union Carbide[4] on their test results on Incoloy 800H and on stainless steel are most likely due to this atmospheric corrosion and not due to the hydrochlorination reaction environment itself.

IV CONCLUSIONS

The experimental results on the hydrochlorination of $SiCl_4$ and m.g. silicon metal show that the hydrochlorination process is an efficient reaction to give good conversion and high yield of $SiHCl_3$. The reaction is very clean and highly specific for the production of $SiHCl_3$. The only significant by-product is a small amount (1-2%) of SiH_2Cl_2 which is also a useful product. Thus, conversion of starting material to useful product is essentially 100%. The effect of pressure on this equilibrium reaction is verified by the experimental data collected at 500 psig These reaction kinetic data reinforce the engineering design of the hydrochlorination reactor for the Union Carbide EPSDU, silane-to-silicon process.

The reaction is well-behaved from a chemical processing point of view. The small heat of reaction generated in the hydrochlorination process[4] is advantageous from a process point of view. The output of a given reactor size can be increased by increasing the reactor pressure. The increases in mass transfer do not

adversely effect the problem of heat transfer since the hydrochlorination reaction is nearly thermal neutral. Furthermore, the nature of the equilibrium reaction practically eliminates the danger of a run away reaction normally associated with a strongly exothermic process. Thus, the relatively poor heat transfer characteristics of a mass bed of silicon metal is not a draw back in the hydrochlorination process. The reaction can be carried out in a fluidized-bed reactor or in a fixed bed reactor.

The presence of a copper catalyst significantly improves the rate of the hydrochlorination reaction. Cuprous chloride is a more efficient catalyst than the cement type copper. The reaction rate is increased by a factor of two with as little as 2 wt% CuCl in the silicon metal mass bed. However, the benefit of a higher production rate in the presence of copper must be balanced by the extra cost accrued from the additional equipment needed to handle the catalyst and from the cost of the copper compound itself. The silicon particle size distribution study produces some interesting results. The reaction rate is essentially independent of the Si particle size within a range of +400 to -32 mesh. This is an advantage from a process point of view since it offers a broader operating latitude for the hydrochlorination process. A highly purified silicon metal gives a much slower reaction rate in comparison with those obtained from the impure, m.g. silicon metal. The small amount of metallic impurities in the 98.5% m.g. silicon metal do not adversely effect the hydrochlorination reaction. In fact,

their presence in the m.g. silicon metal is needed to produce a rapid reaction rate for the hydrochlorination process.

The copper catalyst and the Si particle size distribution studies provided some experimental evidences on the mechanism of the hydrochlorination reaction of $SiCl_4$ and m.g. silicon metal to $SiHCl_3$. The rate-determining step appears to be the adsorption of $SiCl_4$ on the silicon metal surface followed by the reduction of a Si-Cl linkage to SiH with hydrogen. The intermediate by-product HCl produced at the solid surface readily reacts with the Si atoms present to produce $SiHCl_3$. The active catalytic species appears to be the copper-silicon alloys which contain Cu-Si metallic bonds. Free, elemental copper not chemically bonded to the Si on the metal surface is inactive in the hydrochlorination reaction. Crystal defects caused by the presence of copper in the silicon crystal lattics are the plausible mechanism for the observed catalytic activity of copper. This mechanism may also account for the similar catalytic effect of the metallic impurities already present in the m.g. silicon metal in the form of metal silicides. The experimental evidence shows that the hydrochlorination reaction is primarily a gas-solid reaction. A homogeneous gas phase reaction between $SiCl_4$ and hydrogen is either very slow or unlikely.

Results of the prolonged reaction between $SiCl_4$ and m.g. silicon metal in the presence of hydrogen show that the silicon mass bed has a long mass life. This is an important factor in carrying out the hydrochlorination process for long periods of time without interruption. The metallic impurities released from the

reacted m.g. silicon metal particles do not appear to produce harmful effects on the hydrochlorination. Analysis of the elutriated fines provide evidence that these metallic impurities are, at least, partially removed from the Si mass bed by the gas stream passing through the hydrochlorination reactor.

The corrosion studies on Type 304 stainless steel and on Incoloy 800H produce the most gratifying results. At elevated temperatures, HCl is produced in variable amounts in a reaction system containing chlorosilane and hydrogen gas. The highly corrosive effects of HCl on conventional metals and alloys at temperatures above 450°C are well-known. The presence of a protective silicide film at the reactor wall eliminates this potential corrosion problem.

IV RECOMMENDATIONS

(1) Optimum Process Parameters

Based on the reaction kinetic data and on the significant experimental observations, recommendations are made to optimize the reaction parameters for operating the hydrochlorination process. These may include:

- highest practical reaction temperature for the hydrochlorination reaction
- highest practical reactor pressure for the hydrochlorination process
- 2% CuCl catalyst added to the silicon mass bed to improve reaction rate
- conventional nickel-chromium alloys as the material of construction for the hydrochlorination reactor.

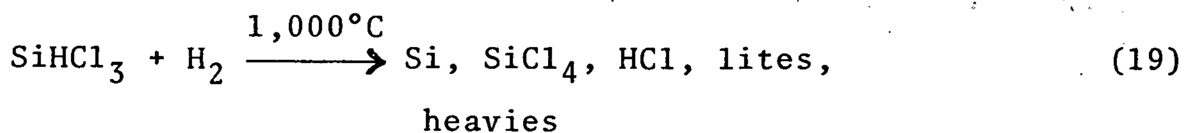
(2) Additional Research and Development for the Hydrochlorination process.

Additional experimental work on the hydrochlorination reaction of $SiCl_4$ and m.g. silicon metal is recommended to further improve the hydrochlorination process in terms of efficiency and cost. This may include:

- further refinement of the reaction kinetic data with a larger reactor size to provide more accurate design criteria for scaling up the hydrochlorination process,
- design experiments to study the fluidization mechanics in a bed of m.g. silicon metal and evaluate the merits between the fluidized-bed and the fixed-bed reactor design,
- additional studies on the effect of impurities, iron and aluminum, on the hydrochlorination reaction and evaluate different grades of commercial silicon metal on a cost-effective basis,
- further corrosion studies to evaluate a variety of commercial metal alloys for the material of construction for the hydrochlorination reaction on a cost-effective basis,
- study the effect of added HCl gas on the hydrochlorination reaction. Residual chloride waste (chlorosilane heavies, $FeCl_3$, $AlCl_3$, etc.) may be hydrolysed and the HCl generated can be fed into the hydrochlorination reactor to produce more useful $SiHCl_3$. The idea to recycle HCl to the hydrochlorination reactor provides a closed-loop scheme for the conventional Siemens Process.

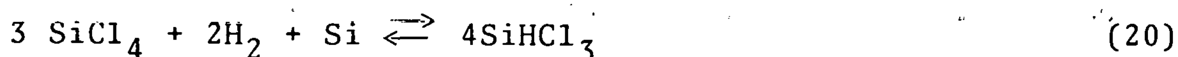
(3) A Closed-Loop Concept for the Siemens Process

The current commercial process for the production of polycrystalline silicon metal involves the vapor phase deposition of silicon metal from a mixture of chlorosilane and hydrogen gas at high temperatures. This is generally known as the Siemens process. Presently, trichlorosilane is the most widely used starting material. The reduction of $SiHCl_3$ in the Siemens type process produces HCl and $SiCl_4$ as the major by-products.



$$SiHCl_3 + H_2 \xrightarrow{1,000°C} Si, SiCl_4, HCl, \text{lites, heavies} \quad (19)$$

The need to handle and to dispose of these by-products results in a large negative impact on the economics of the Siemens type process for the production of polycrystalline silicon metal used by the electronics industry. Furthermore, only part of the silicon is deposited. A significant portion of the starting $SiHCl_3$ is lost as by-product $SiCl_4$. The hydrochlorination of $SiCl_4$ and m.g. silicon metal,

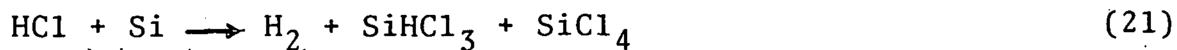


$$3\ SiCl_4 + 2H_2 + Si \rightleftharpoons 4SiHCl_3 \quad (20)$$

provide a perfect fit in a closed-loop concept to recycle these by-products.

This closed-loop Siemens Process for the production of polycrystalline silicon metal is illustrated in Figure XXVIII. The block diagram at the left represents the Siemens type reactor which generates the product polycrystalline silicon metal and the by-product stream, HCl, $SiCl_4$, Si-Si and Si-Cl. The Si-Si

represents the heavies in Equation (19) which consists mostly disilane ($Cl_3SiSiCl_3$) and polysilanes. The Si-Cl represents the lites in Equation (19) which consist of mainly lower boiling SiH_2Cl_2 and SiH_3Cl. The hydrochlorination reaction (Equation 20) fits perfectly into the closed-cycle scheme as shown in Figure XXVIII. First of all, it produces the starting $SiHCl_3$ for the Siemens reactor. Secondly, it consumes the by-product $SiCl_4$ generated by the Siemens Process. Thirdly, the same hydrochlorination reactor can be used to recycle HCl to produce more $SiHCl_3$, viz.,



$$HCl + Si \longrightarrow H_2 + SiHCl_3 + SiCl_4 \qquad (21)$$

The well-known HCl + Si reaction (Equation 21) produces $SiHCl_3$ and H_2 with a minor amount of $SiCl_4$. The $SiCl_4$ and H_2 are also the starting material for the hydrochlorination reaction. Furthermore, even the remaining small amount of by-products (lites and heavies) from the Siemens reaction can be recycled to the hydrochlorination reactor. At 500°C and in the presence of hydrogen, the Si-Si linkages are reduced to SiH, viz.,

$$Cl_3SiSiCl_3 + H_2 \longrightarrow 2\ SiHCl_3 \qquad (22)$$

At 500°C, the lites (SiH_2Cl_2, SiH_3Cl) are readily redistributed to the more thermally stable $SiCl_4$ and $SiHCl_3$. In essence, all the by-products, major and minor, coming out of the Siemens reactor can be, at least in principle, converted back to $SiHCl_3$ in the same hydrochlorination reactor as shown in Figure XXVIII.

A distillation/separation step separates the chlorosilane components and the hydrogen gas. Unreacted $SiCl_4$ is recycled back to the hydrochlorination reactor. The $SiHCl_3$ and a small amount of SiH_2Cl_2 are fed back to the Siemens reactor with the hydrogen gas after a purification step to up-grade their purity requirements for the production of electronic grade silicon metal.

This closed-cycle Siemens production scheme utilizes the impure m.g. silicon metal as the only starting material while it produces polycrystalline silicon metal as the only product. The chlorine and hydrogen are merely intermediate carriers to affect the purification of the m.g. silicon metal. Therefore, substantial savings on the raw material cost can be realized.

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VII APPENDICES

Table I through Table XXVII.

Figure I through Figure XXVIII.

TABLE I

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

Experiment No.	Hydrogen Feedrate SCCM[1]	Residence Time Second	Reaction SiH_2Cl_2	Product mole% $SiHCl_3$	Composition[2] $SiCl_4$
1A	4088	22.2	0.469	21.96	77.58
2A	2717	33.4	0.556	24.44	75.00
3A	2203	41.2	0.764	26.99	72.25
4A	1388	65.4	0.954	29.47	69.58
1B	1290	65.3	1.19	32.19	66.63
2B	925	91.1	1.29	33.36	65.36
3B	720	117	1.39	34.04	64.57
1C	662	117	1.55	35.04	63.41
D	470	193	1.52	35.42	63.06
4B	393	215	1.40	35.62	62.94
2C	345	224	1.74	37.12	61.14
3C	180	429	1.89	38.45	59.67

(1) SCCM Standard C.C. per minute

(2) Average of two or three analyses

TABLE II

HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 500 PSIG, 450°C AND $H_2/SiCl_4$ RATIO OF 2.8

Experiment No.	Hydrogen Feedrate SCCM(1)	Residence Time Second	Reaction	Product mole%	Composition(2)
			SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	2920	20.7	<0.05	12.54	87.48
2	2045	29.6	0.064	15.87	84.06
3	1675	36.1	0.140	17.60	82.29
4	1530	42.1	0.232	18.99	80.89
5	1215	53.0	0.393	21.15	78.46
6	1020	63.1	0.651	22.75	76.60
7	477	135	0.969	29.83	69.20
8	235	257	1.224	33.38	65.40

(1) SCCM, Standard C.C. per minute

(2) Average of two or three analyses

TABLE III

HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON
AT 500 PSIG, 550°C AND $H_2/SiCl_4$ RATIO OF 2.8

Experiment No.	Hydrogen Feedrate SCCM	Residence Time Second	Reaction SiH_2Cl_2	Product mole% $SiHCl_3$	Composition $SiCl_4$
1	2948	17.7	0.770	28.49	70.74
			0.807	28.44	70.75
2	1465	35.7	1.239	33.69	65.08
			1.315	33.99	64.70
3	813	64.3	1.772	35.83	62.40
			1.795	35.86	62.35
4	409	128	2.356	38.52	59.13
			2.387	38.19	59.42
5	277	189	2.537	39.38	58.08
			2.685	39.54	57.77
6	214	244	2.798	40.48	56.73
			2.761	40.32	56.92

TABLE IV

HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON

AT 300 PSIG, 550°C AND $H_2/SiCl_4$ RATIO OF 1.0

Experiment No.	Hydrogen Feedrate SCCM	Residence Time Second	Reaction SiH_2Cl_2	Product mole% $SiHCl_3$	Composition $SiCl_4$
1	1850	12.8	0.420	21.32	78.27
			0.383	20.77	78.85
2	1157	20.5	0.702	25.90	73.40
			0.644	25.20	74.16
3	737	32.2	1.021	29.38	69.60
			0.973	29.10	69.94
4	415	57.2	1.124	30.78	68.09
			1.127	30.29	68.59
			1.117	30.28	68.61
5	222	107	1.334	33.28	65.39
			1.426	33.44	65.13

TABLE V

HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 300 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 1.0

Experiment No.	Hydrogen Feedrate SCCM	Residence Time Second	Reaction Product mole% Composition SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	2606	11.7	0.090	12.84	86.26
			0.083	13.09	86.08
2	1879	16.2	0.211	16.71	83.07
			0.208	16.73	83.06
3	1288	23.6	0.351	20.39	79.26
			0.343	20.06	79.60
4	793	38.4	0.476	23.23	76.30
			0.477	23.12	76.41
5	426	71.5	0.701	25.97	73.33
			0.700	26.22	73.08
6	140	218	0.994	29.52	69.49
			1.030	29.44	69.53

TABLE VI

HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON
AT 300 PSIG, 450°C AND $H_2/SiCl_4$ RATIO OF 1.0

Experiment No.	Hydrogen Feedrate	Residence Time	Reaction Product Composition mole%		
	SCCM	Second	SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	2485	12.3	~0	8.166	91.84
2	1900	16.0	0.026	10.08	89.90
3	1323	23.0	0.096	12.83	87.07
4	926	32.9	0.190	16.41	83.46
5	483	63.0	0.298	19.16	80.55
6	382	79.7	0.349	20.61	79.05
7	178	171	0.609	24.47	74.93

TABLE VII

HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON
AT 300 PSIG 400°C AND $H_2/SiCl_4$ RATIO OF 1.0

Experiment No.	Hydrogen Feedrate SCCM	Residence Time Second	Reaction SiH_2Cl_2	Product mole% $SiHCl_3$	Composition $SiCl_4$
1	1981	15.4	~0	5.030	94.97
2	1313	23.2	~0	7.501	92.50
3	766	39.8	0.026	10.65	89.33
4	394	77.4	0.065	14.28	85.66
5	157	194	0.303	21.23	78.46

TABLE VIII

HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON
AT 300 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 2.8

Experiment No.	Hydrogen Feedrate SCCM	Residence Time Second	Reaction SiH_2Cl_2	Product mole% $SiHCl_3$	Composition $SiCl_4$
1	2747	17.3	0.312	20.38	79.31
2	1887	25.3	0.557	24.95	74.50
3	1545	30.8	0.711	26.79	72.50
4	1200	39.7	0.873	28.76	70.38
5	845	56.4	1.138	31.98	66.89
6	540	88.3	1.342	33.46	65.19
7	275	173	1.674	35.47	62.85

TABLE IX

HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON

AT 300 PSIG, 450°C AND $H_2/SiCl_4$ RATIO OF 2.8

Experiment No.	Hydrogen Feedrate SCCM	Residence Time Second	Reaction Product Composition mole% SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	2717	19.4	0.154	15.14	84.71
2	1820	28.9	0.268	18.70	81.03
3	1273	41.3	0.403	21.97	77.63
4	884	59.5	0.541	24.72	74.75
5	680	77.4	0.650	26.70	72.64
6	455	116	0.860	28.55	70.56
7	263	200	1.070	31.32	67.61

TABLE X

HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON

AT 300 PSIG, 400°C AND $H_2/SiCl_4$ RATIO OF 2.8

Experiment No.	Hydrogen Feedrate	Residence Time	Reaction	Product mole%	Composition
	SCCM	Second	SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	2454	21.7	~ 0	8.519	91.48
2	1640	32.4	<0.02	12.52	87.49
3	838	63.4	0.063	14.96	84.98
4	485	110	0.324	20.41	79.27
5	219	243	0.663	25.26	74.08

TABLE XI

HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON
AT 500 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 2.8
WITH 5% CEMENT COPPER

Experiment No.	Hydrogen Feedrate SCCM [1]	Residence Time Second	Reaction SiH_2Cl_2	Product mole% [2] $SiHCl_3$	Composition $SiCl_4$
1	1735	34.9	1.005	30.06	68.91
2	1195	50.6	1.126	33.56	65.31
3	790	76.5	1.277	35.50	63.23
4	395	153	1.305	36.26	62.44
5	210	288	1.482	38.10	60.42

(1) SCCM, Standard c.c. per minute

(2) Average of two or three analyses

TABLE XII

HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON
AT 500 PSIG, 450°C AND $H_2/SiCl_4$ RATIO OF 2.8
WITH 5% CEMENT COOPER

Experiment No.	Hydrogen Feedrate SCCM[1]	Residence Time Second	Reaction SiH_2Cl_2	Product mole%[2] $SiHCl_3$	Composition $SiCl_4$
1	1715	34.9	0.711	24.02	75.28
2	1105	54.2	0.856	29.06	70.09
3	657	91.2	0.968	31.88	67.16
4	390	154	1.148	33.86	64.99
5	193	310	1.290	35.79	62.92

(1) SCCM, Standard c.c. per minute

(2) Average of two or three analyses

TABLE XIII

HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 300 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 1.0 WITH 5% CEMENT COPPER

Experiment No.	Hydrogen Feedrate SCCM (1)	Residence Time Second	Reaction SiH_2Cl_2	Product mole% (2) $SiHCl_3$	Composition $SiCl_4$
1	1552	13.7	0.616	21.12	78.53
2	1158	18.3	0.622	21.72	77.66
3	705	30.1	0.719	23.67	75.61
4	382	55.5	0.792	27.02	72.19
5	187	113	1.049	29.18	69.77

(1) SCCM, Standard c.c. per minute

(2) Average of two or three analyses

TABLE XIV

HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON
AT 300 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 2.8
WITH 5% CEMENT COPPER

Experiment No.	Hydrogen Feedrate SCCM (1)	Residence Time Second	Reaction SiH_2Cl_2	Product mole% (2) $SiHCl_3$	Composition $SiCl_4$
1	1750	16.6	0.861	28.19	70.95
2	1288	22.6	0.969	29.91	69.13
3	690	42.1	1.125	33.06	65.82
4	386	75.4	1.416	35.21	63.37
5	150	194	1.626	38.06	60.31

(1) SCCM, Standard c.c. per minute

(2) Average of two or three analyses

TABLE XV

HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON
AT 500 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 2.8
WITH 5% CUPROUS CHLORIDE

Experiment No.	Hydrogen Feedrate SCCM (1)	Residence Time Second	Reaction Product mole% (2) SiH_2Cl_2	$SiHCl_3$	Composition $SiCl_4$
1	1780	44.9	1.404	34.13	64.47
2	1246	64.2	1.450	37.98	60.57
3	770	104	1.610	39.23	59.16
4	370	216	1.977	41.28	56.74
5	237	338	2.271	41.38	56.35

(1) SCCM, Standard c.c. per minute

(2) Average of two or three analyses

TABLE XVI

HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON
AT 500 PSIG, 450°C AND $H_2/SiCl_4$ RATIO OF 2.8
WITH 5% CUPROUS CHLORIDE

Experiment No.	Hydrogen Feedrate SCCM [1]	Residence Time Second	Reaction Product mole% [2] SiH_2Cl_2	$SiHCl_3$	Composition $SiCl_4$
1	1782	46.4	0.925	29.93	69.14
2	1244	66.5	1.240	32.88	65.89
3	692	120	1.504	35.32	63.18
4	382	216	1.446	38.92	59.63
5	222	373	2.074	39.39	58.54

(1) SCCM, Standard c.c. per minute

(2) Average of two or three analyses

TABLE XVII

HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON
AT 300 PSIG, 500°C AND $H_2/SiCl_4$ RATIO OF 1.0
WITH 5% CUPROUS CHLORIDE

Experiment No.	Hydrogen Feedrate SCCM (1)	Residence Time Second	Reaction SiH_2Cl_2	Product mole% (2) $SiHCl_3$	Composition $SiCl_4$
1	1550	18.2	0.461	21.86	77.68
2	1037	27.2	0.574	23.63	75.81
3	700	40.2	0.923	26.55	72.53
4	390	72.2	0.944	28.64	70.42
5	147	192	1.311	31.02	67.68

(1) SCCM, Standard c.c. per minute

(2) Average of two or three analyses

TABLE XVIII

HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON
AT 300 PSIG, 400°C AND $H_2/SiCl_4$ RATIO OF 1.0
WITH 5% CUPROUS CHLORIDE

Experiment No.	Hydrogen Feedrate SCCM (1)	Residence Time Second	Reaction Product mole% (2) SiH_2Cl_2	Composition $SiHCl_3$	$SiCl_4$
1	1908	18.3	0.078	9.91	90.02
2	1406	24.8	0.100	11.42	88.49
3	789	44.1	0.189	15.94	83.88
4	458	76.0	0.277	19.09	80.64
5	254	137	0.435	21.92	77.65
6	135	258	0.599	25.90	73.50

(1) SCCM, Standard c.c. per minute

(2) Average of two or three analyses

TABLE XIX

HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON
AT 300 PSIG, 500°C AND $H_2/SiCl_4$ = 1.0 WITH 2% CuCl

Experiment No.	Hydrogen Feedrate SCCM (1)	Residence Time Second	Reaction SiH_2Cl_2	Product mole% $SiHCl_3$	Composition $SiCl_4$
1	1350	21.5	0.4644	21.98	77.56
2	940	30.9	0.5206	23.58	75.91
3	620	46.8	0.7516	27.05	72.21
4	220	132	1.040	30.25	68.71

(1) SCCM, Standard c.c. per minute

TABLE XX

PARTICLE SIZE DISTRIBUTION OF M.G. SILICON METAL

FOR THE HYDROCHLORINATION STUDIES

Tyler Mesh No.	Particle Size Range µm (1)	Mean Particle Size µm	Relative Surface Area 65 x 150 = 1.0	Bulk Density Compact g./c.c	Bulk Density Loose g./c.c	Average Density g./c.c	% Void Space
32 x 65	500 x 210	355	0.45	1.39	1.29	1.34	43
65 x 150	210 x 105	158	1.00	1.24	1.14	1.19	49
150 x 400	105 x 37	71	2.23	1.24	1.07	1.16	50

(1) µm, micrometer = microns

TABLE XXI

HYDROCHLORINATION OF $SiCl_4$ WITH 32 x 65 MESH M.G. Si AT 500 PSIG, 500°C AND $H_2/SiCl_4$ = 2.8

Experiment No.	Hydrogen Feedrate SCCM (1)	Residence Time Second	Reaction SiH_2Cl_2	Product mole% $SiHCl_3$	Composition $SiCl_4$
1	1767	28.8	0.615	25.16	74.23
2	1186	42.9	0.786	27.88	71.34
3	618	82.3	1.004	31.44	67.56
4	328	155	1.273	33.30	65.43
5	175	290	1.162	35.09	63.75

(1) SCCM, Standard c.c. per minute

TABLE XXII

HYDROCHLORINATION OF $SiCl_4$ AND 150 x 400 MESH M.G. Si AT 500 PSIG, 500°C AND $H_2/SiCl_4$ - 2.8

Experiment No.	Hydrogen Feedrate SCCM[1]	Residence Time Second	Reaction SiH_2Cl_2	Product mole% $SiHCl_3$	Composition $SiCl_4$
1	1489	50.9	1.086	31.18	67.74
2	1015	75.2	1.190	33.52	65.29
3	649	118	1.218	34.20	64.59
4	347	220	1.564	36.20	62.24
5	191	400	1.723	37.84	60.44

(1) SCCM, Standard c.c. per minute

TABLE XXIII

HYDROCHLORINATION OF $SiCl_4$ AND 150 x 400 MESH M.G. Si AT 300 PSIG, 500°C AND $H_2/SiCl_4$ = 1.0

Experiment No.	Hydrogen Feedrate SCCM[1]	Residence Time Second	Reaction SiH_2Cl_2	Product mole% $SiHCl_3$	Composition $SiCl_4$
1	1058	32.7	0.3501	20.52	79.13
2	716	48.3	0.4318	21.79	77.79
3	425	81.3	0.5152	24.62	74.86
4	168	206	0.6550	25.76	73.59

(1) SCCM, Standard c.c. per minute

TABLE XXIV

HYDROCHLORINATION OF $SiCl_4$ AND 32 x 65 MESH
M.G. Si AT 300 PSIG, 500°C AND $H_2/SiCl_4$ = 1.0

Experiment No.	Hydrogen Feedrate SCCM (1)	Residence Time Second	Reaction SiH_2Cl_2	Product mole% $SiHCl_3$	Composition $SiCl_4$
1	1760	12.9	0.1527	14.55	85.30
2	1230	18.5	0.2137	17.00	82.78
3	626	36.4	0.2784	20.50	79.23
4	315	72.3	0.4356	23.19	76.38
5	158	144	0.5277	24.63	74.84

(1) SCCM, Standard c.c. per minute

TABLE XXV

HYDROCHLORINATION OF $SiCl_4$ AND ELECTRONIC GRADE Si TO $SiHCl_3$ AT 500 PSIG, 500°C AND $H_2/SiCl_4$ Ratio of 2.8

Experiment No.	Hydrogen Feedrate SCCM(1)	Residence Time Second	Reaction SiH_2Cl_2	Product mole% $SiHCl_3$	Composition $SiCl_4$
1	1200	71.3	0.2982	10.19	89.51
2	800	107	0.3507	12.71	86.94
3	415	207	0.2990	16.86	82.84
4	205	419	0.6389	25.70	73.66

(1) SCCM, Standard c.c. per minute

TABLE XXVI

HYDROCHLORINATION OF $SiCl_4$ AND ELECTRONIC GRADE
Si METAL WITH 5% CuCl ADDED AT 500 PSIG,
500°C AND $H_2/SiCl_4$ = 2.8

Experiment No.	Hydrogen Feedrate SCCM[(1)]	Residence Time Second	Reaction Product Composition mole% SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	1417	50.1	1.756	34.58	63.67
2	1009	70.4	1.652	36.32	62.03
3	542	131	1.817	38.40	59.78
4	309	231	1.704	40.08	58.21

(1) SCCM, Standard c.c. per minute

TABLE XXVII

HYDROCHLORINATION OF $SiCl_4$ AND M.G. Si AT 500°C,

300 PSIG AND $H_2/SiCl_4$ = 2.0

Experiment Date	Cumulative Reaction Time Hour	Silicon Mass Bed g.	Hydrogen Feedrate SCCM	Residence Time Second	SiH_2Cl_2 mole%	$SiHCl_3$ mole%
8/28/80	25	151.7	1340	31.2	0.4084	22.30
9/10/80	65	136.4	1146	32.8	0.3641	22.53
10/20/80	155	126.3	1070	32.5	0.4809	22.10
10/28/80	183	129.8	1080	33.1	0.4049	21.87
11/07/80	229	129.5	1090	32.7	0.4357	22.35

FIGURE 1 Apparatus For The Hydrogenation Of $SiCl_4$ To $SiHCl_3$

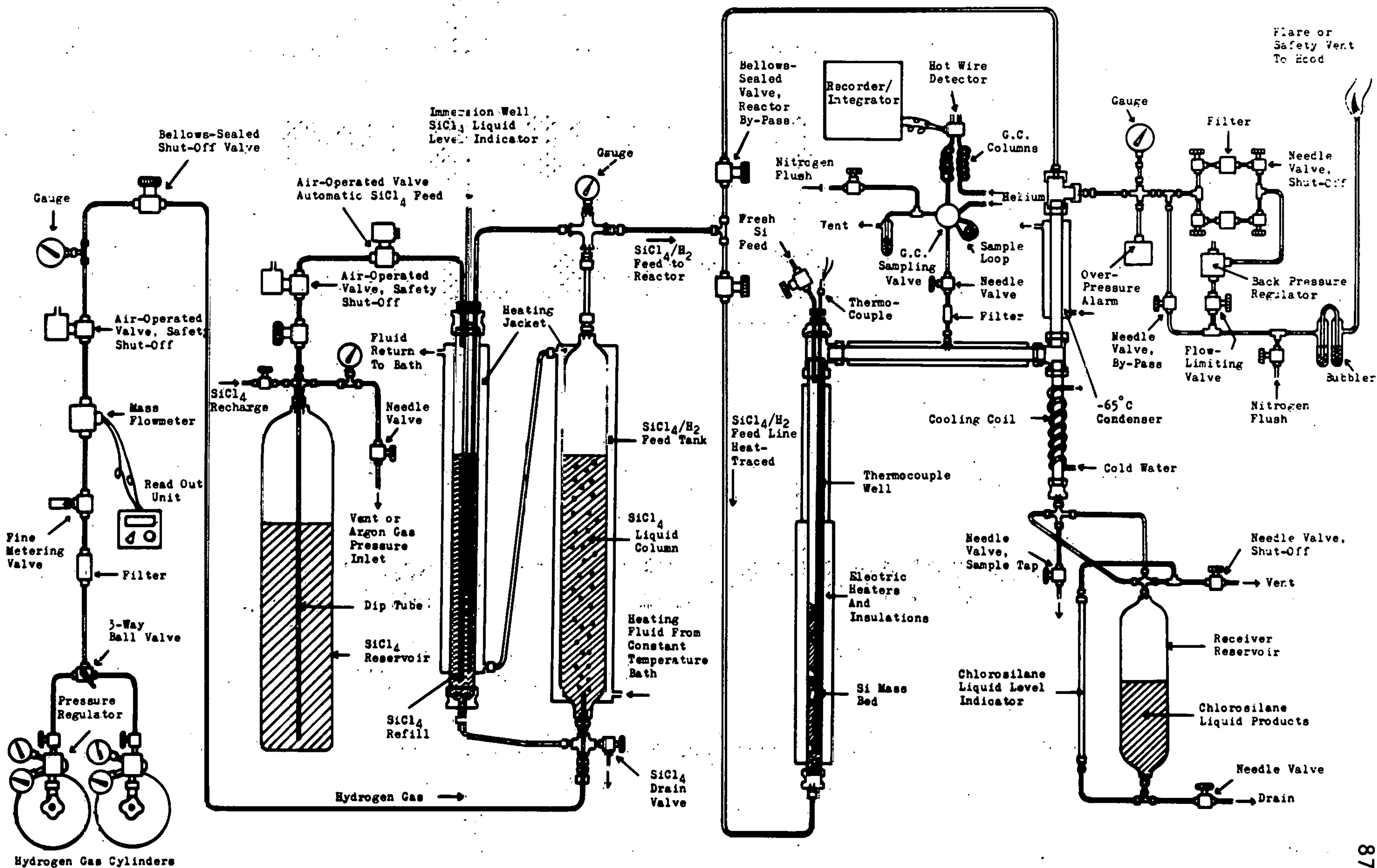
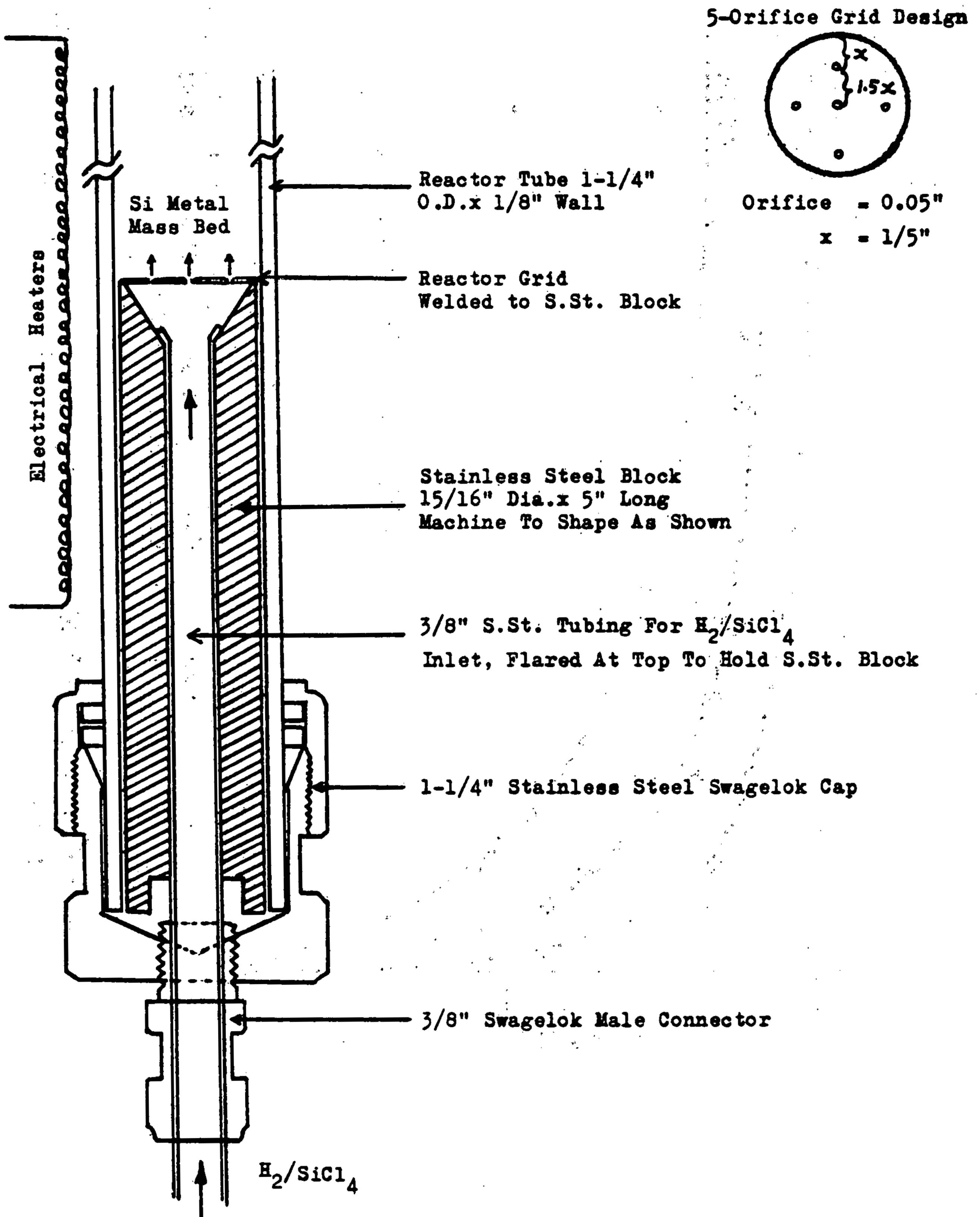


FIGURE II $H_2/SiCl_4$ Gaseous Inlet to Reactor and Grid Design



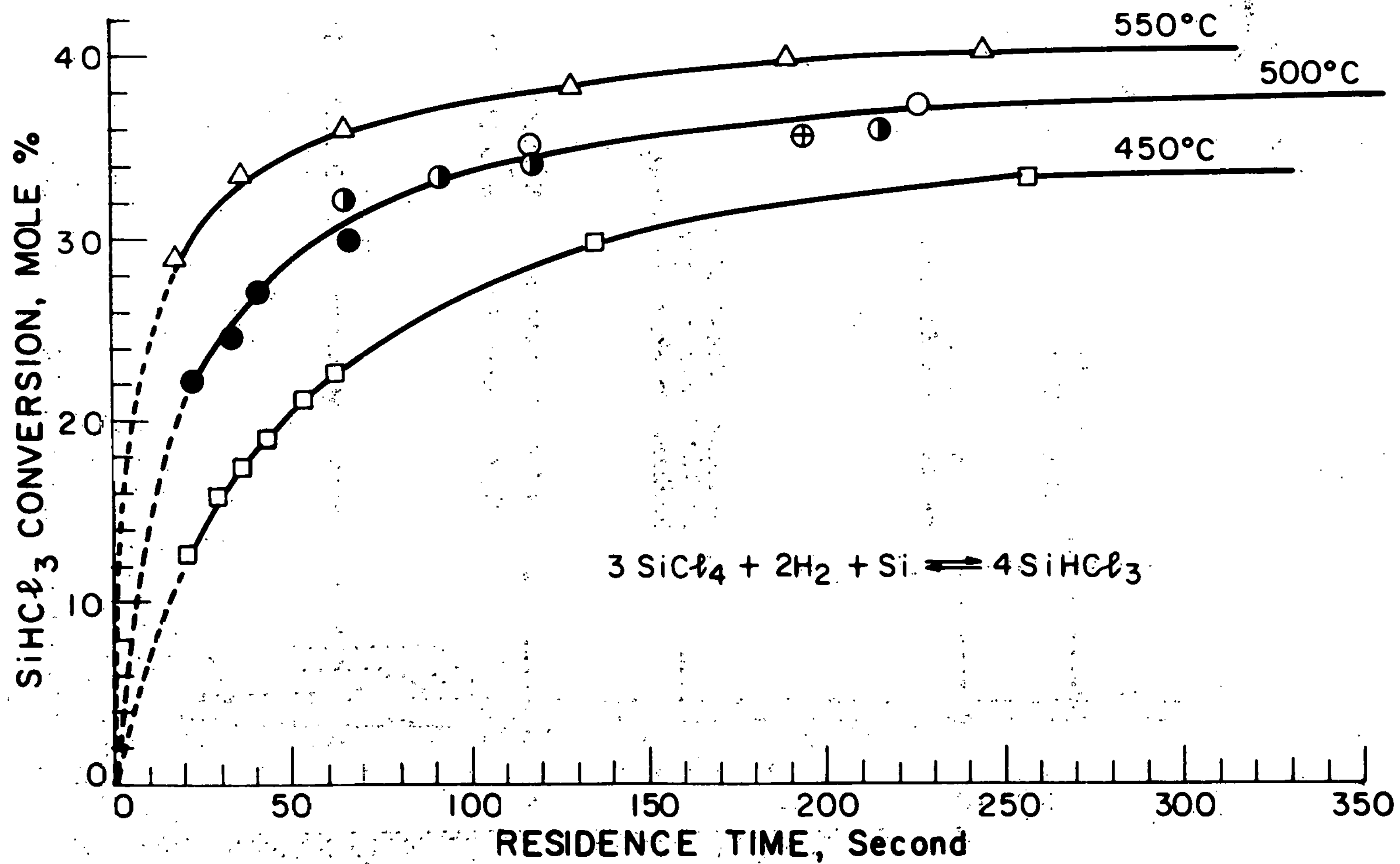


FIGURE III HYDROCHLORINATION OF $SiCl_4$ AT 500 PSIG, $H_2/SiCl_4$ RATIO OF 2.8

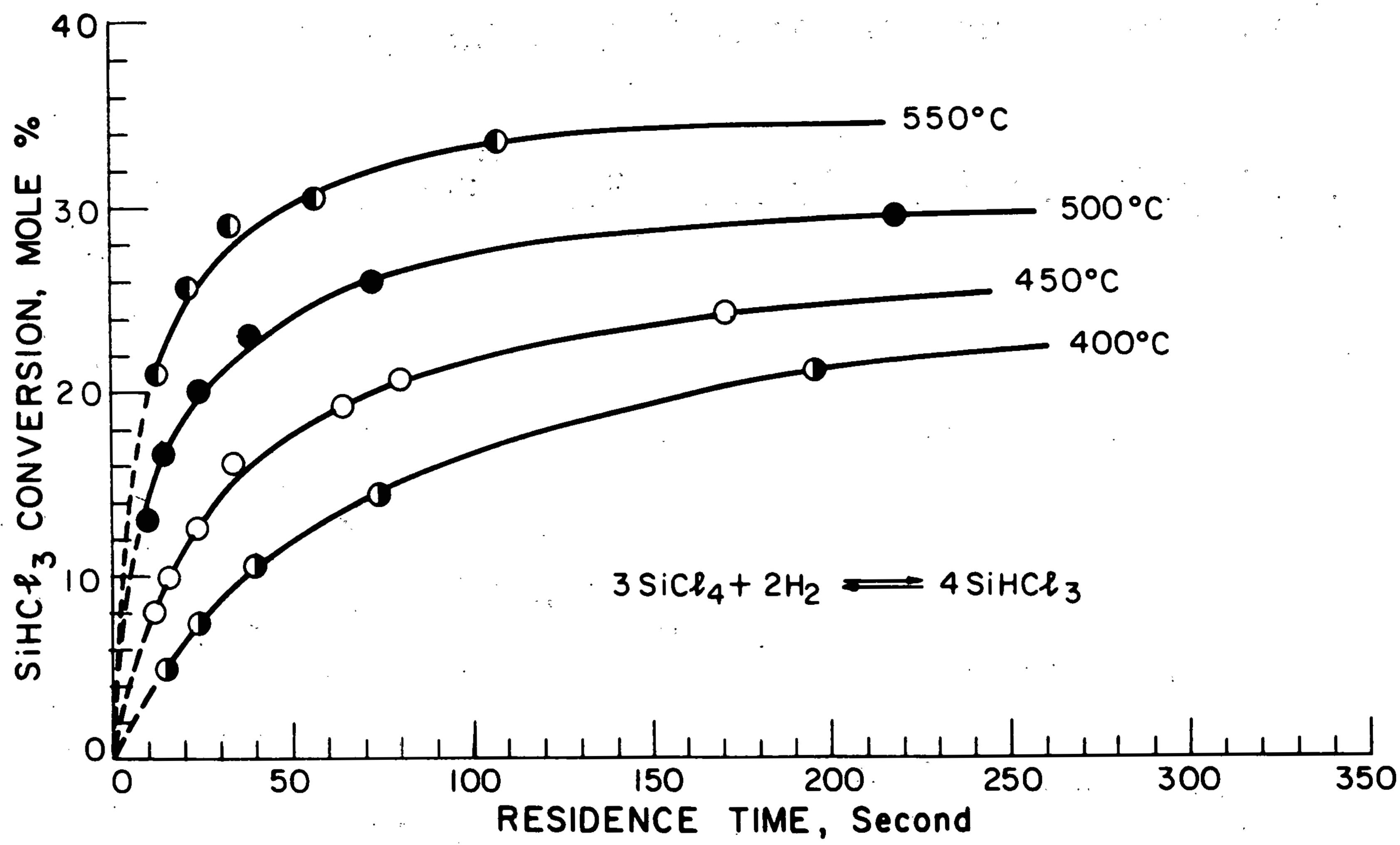


FIGURE IV HYDROCHLORINATION OF $SiC\ell_4$ AT 300 PSIG, $H_2/SiC\ell_4$ RATIO OF 1.0

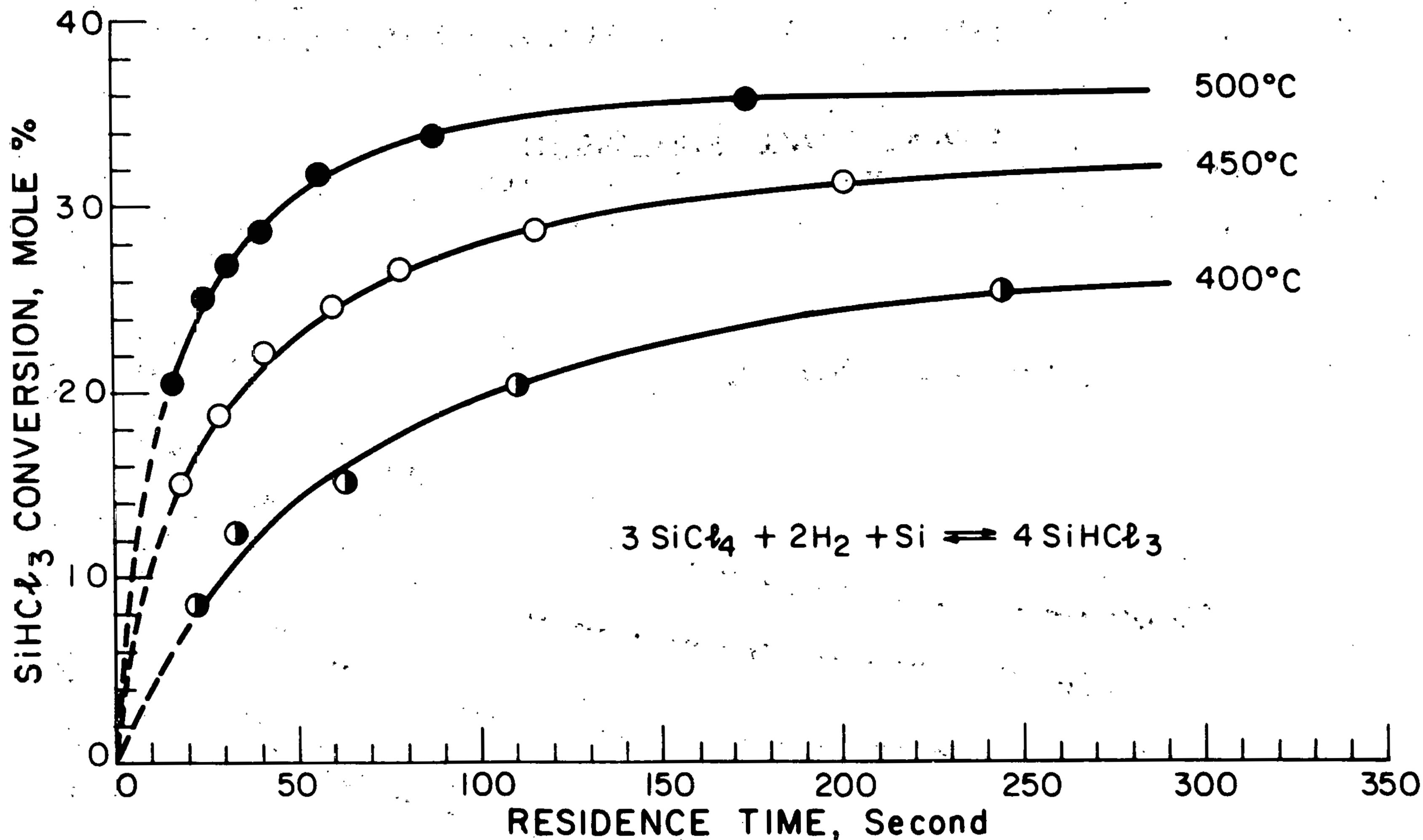


FIGURE V HYDROGENATION OF $SiCl_4$ AT 300 PSIG AND $H_2/SiCl_4$ RATIO OF 2.8

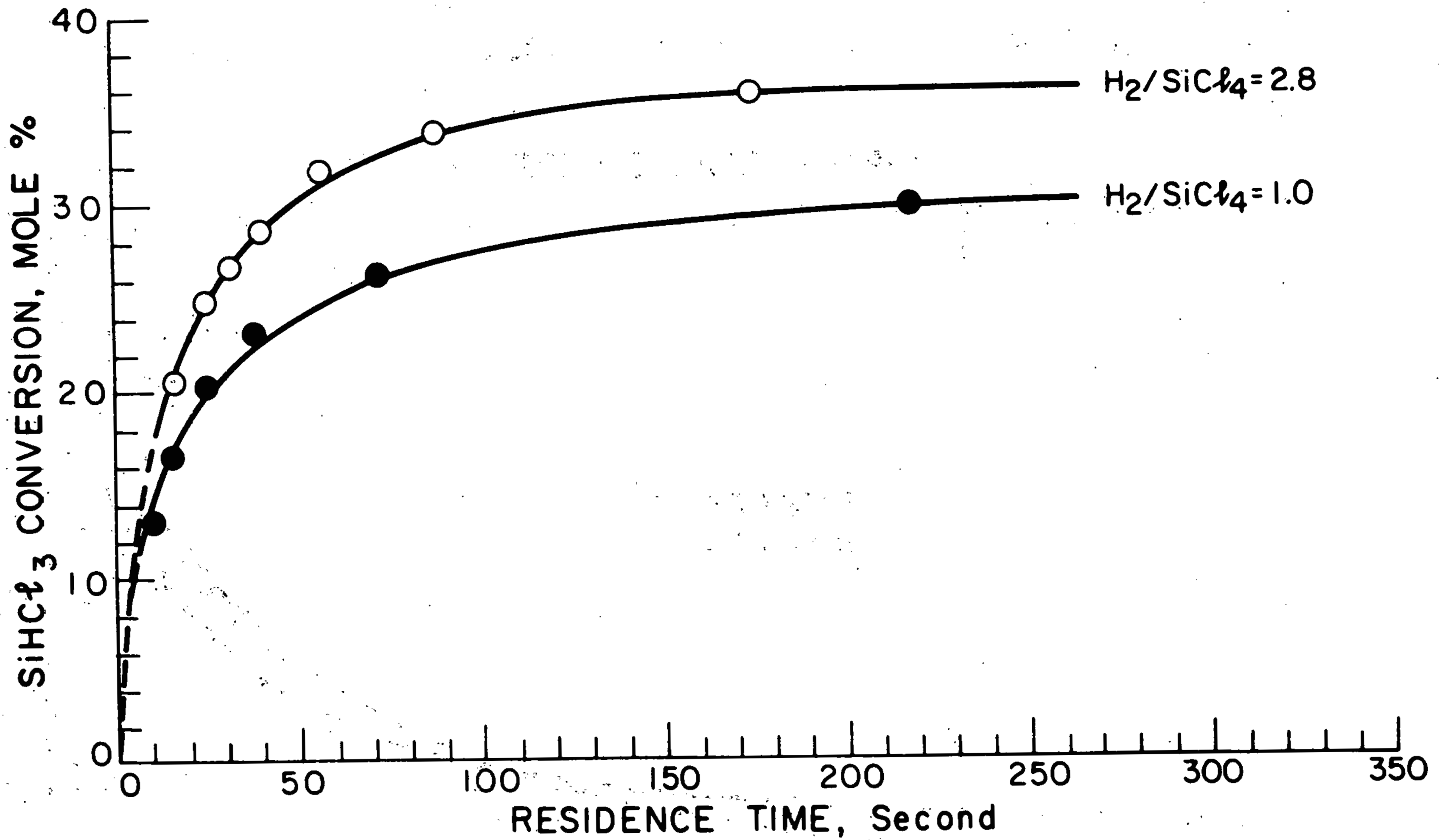


FIGURE VI EFFECT OF H_2 : $SiCl_4$ RATIO AT 500°C, 300 PSIG

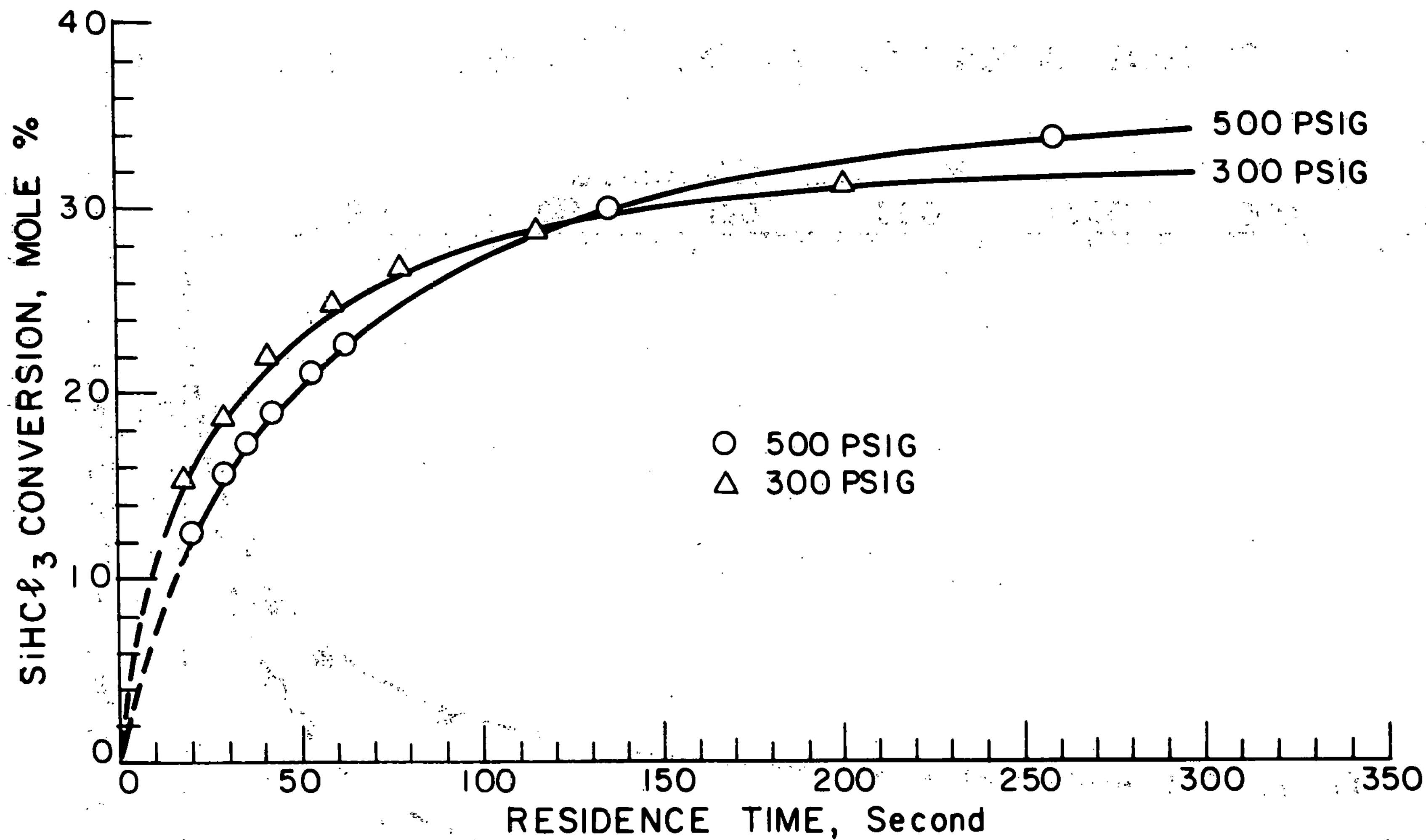


FIGURE VII EFFECT OF PRESSURE ON THE REACTION RATE AT 450°C, $H_2/SiCl_4$ RATIO OF 2.8

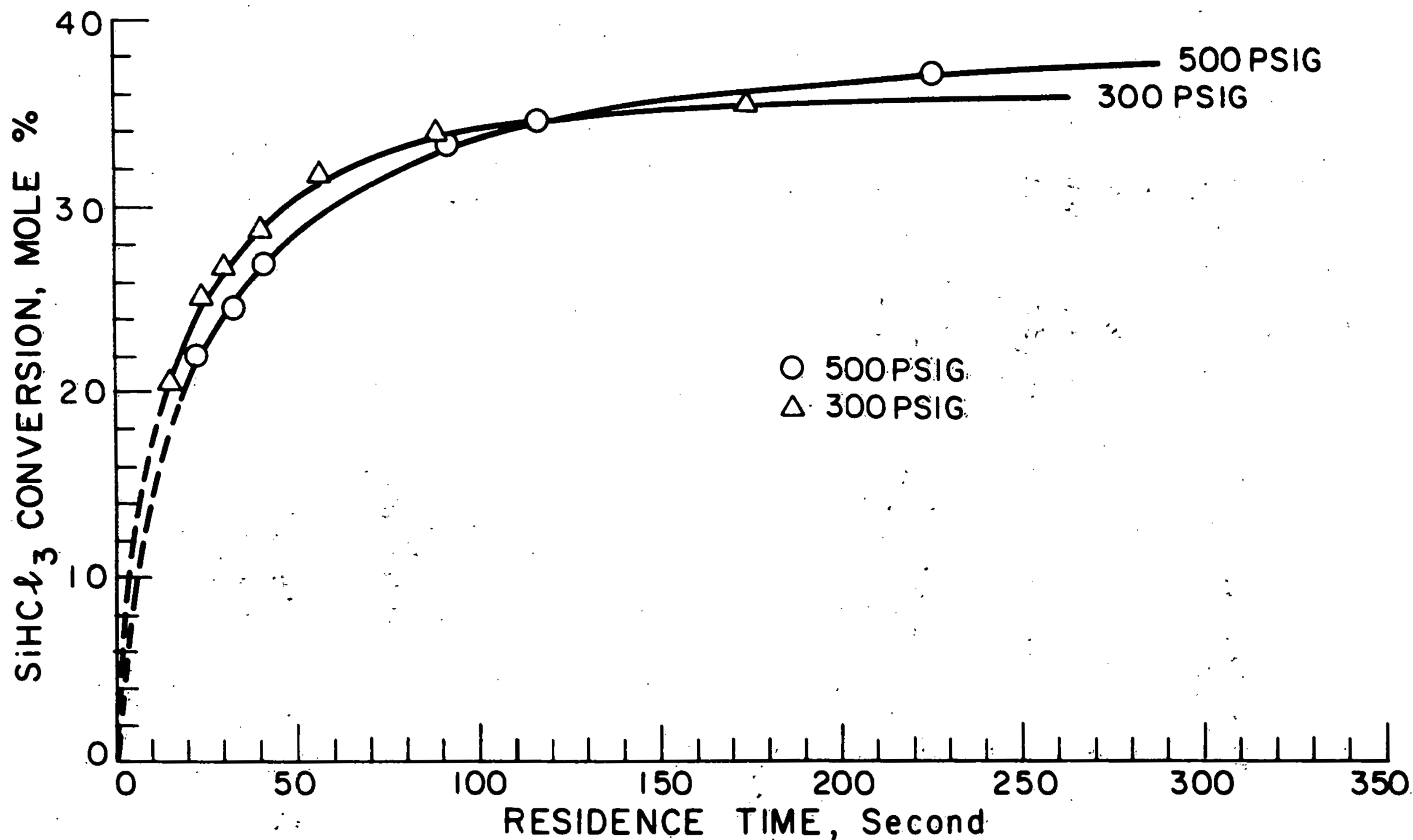


FIGURE VIII EFFECT OF PRESSURE ON THE REACTION RATE AT 500°C, $H_2/SiCl_4$ RATIO OF 2.8

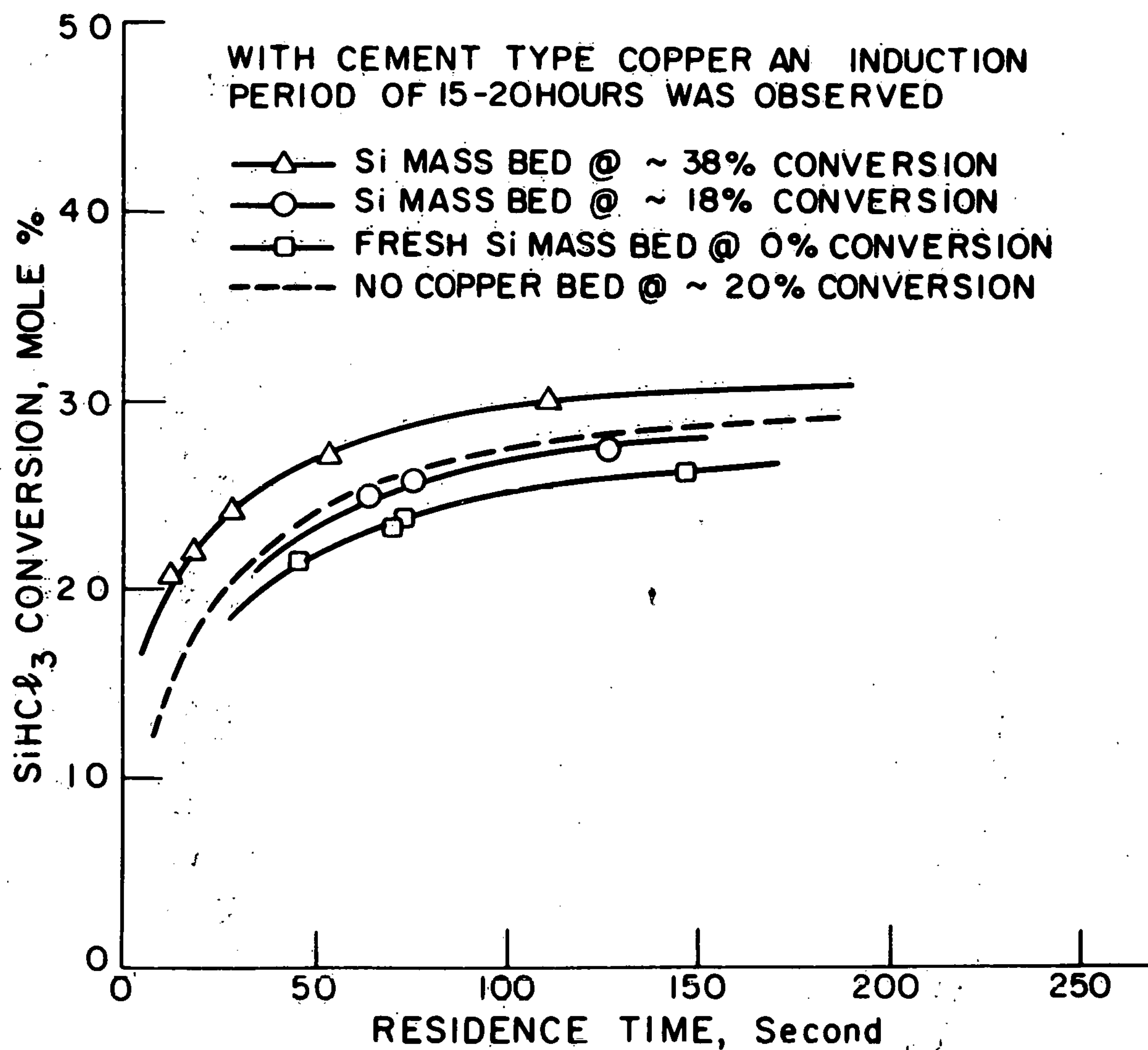


FIGURE IX HYDROCHLORINATION OF $SiC\ell_4$ AT 300 PSIG, 500°C AND $H_2/SiC\ell_4$ = 1.0 WITH 5% CEMENT COPPER CATALYST

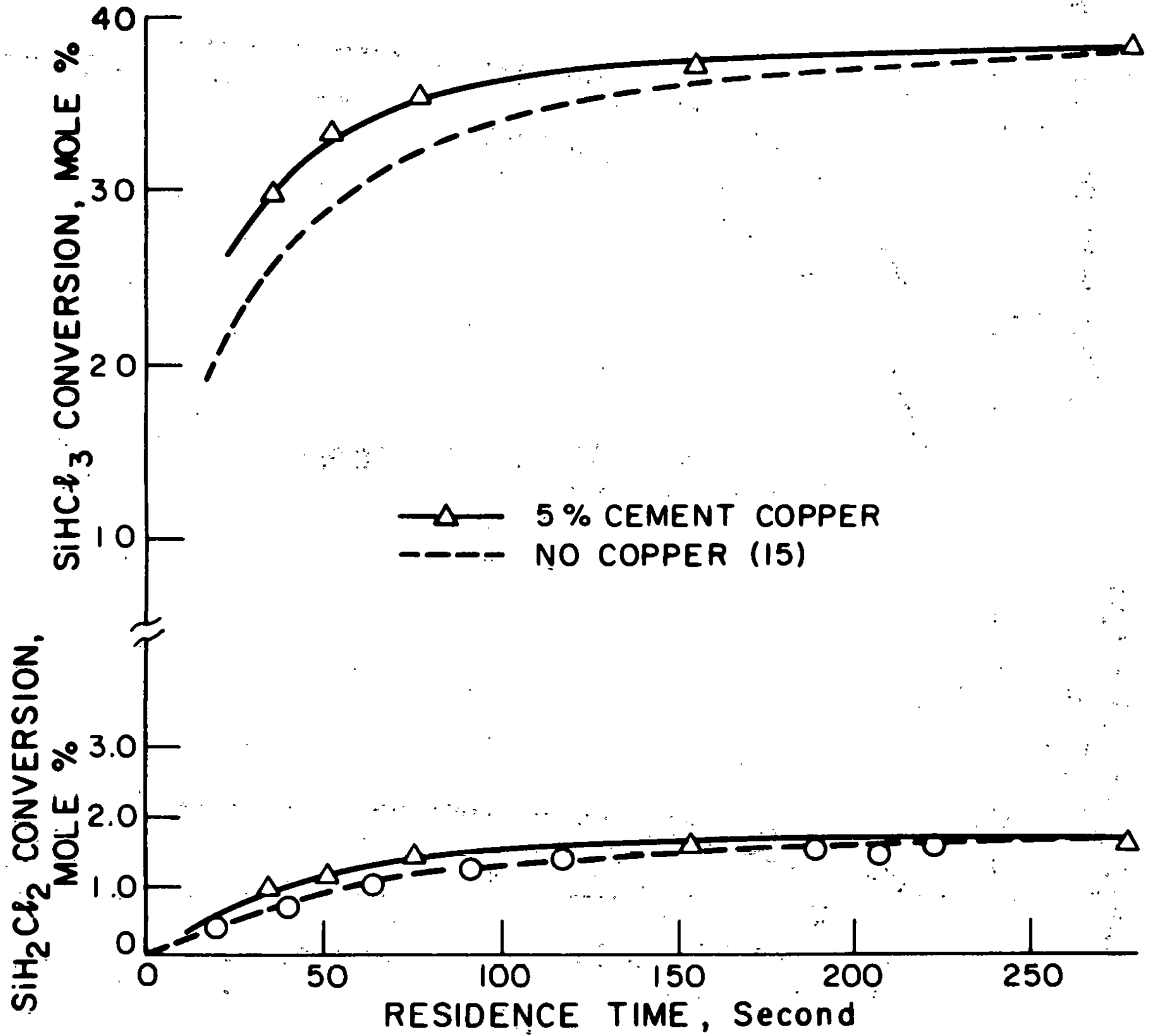


FIGURE X HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON AT 500 PSIG, 500°C AND $H_2/SiCl_4$ = 2.8 WITH 5% CEMENT COPPER

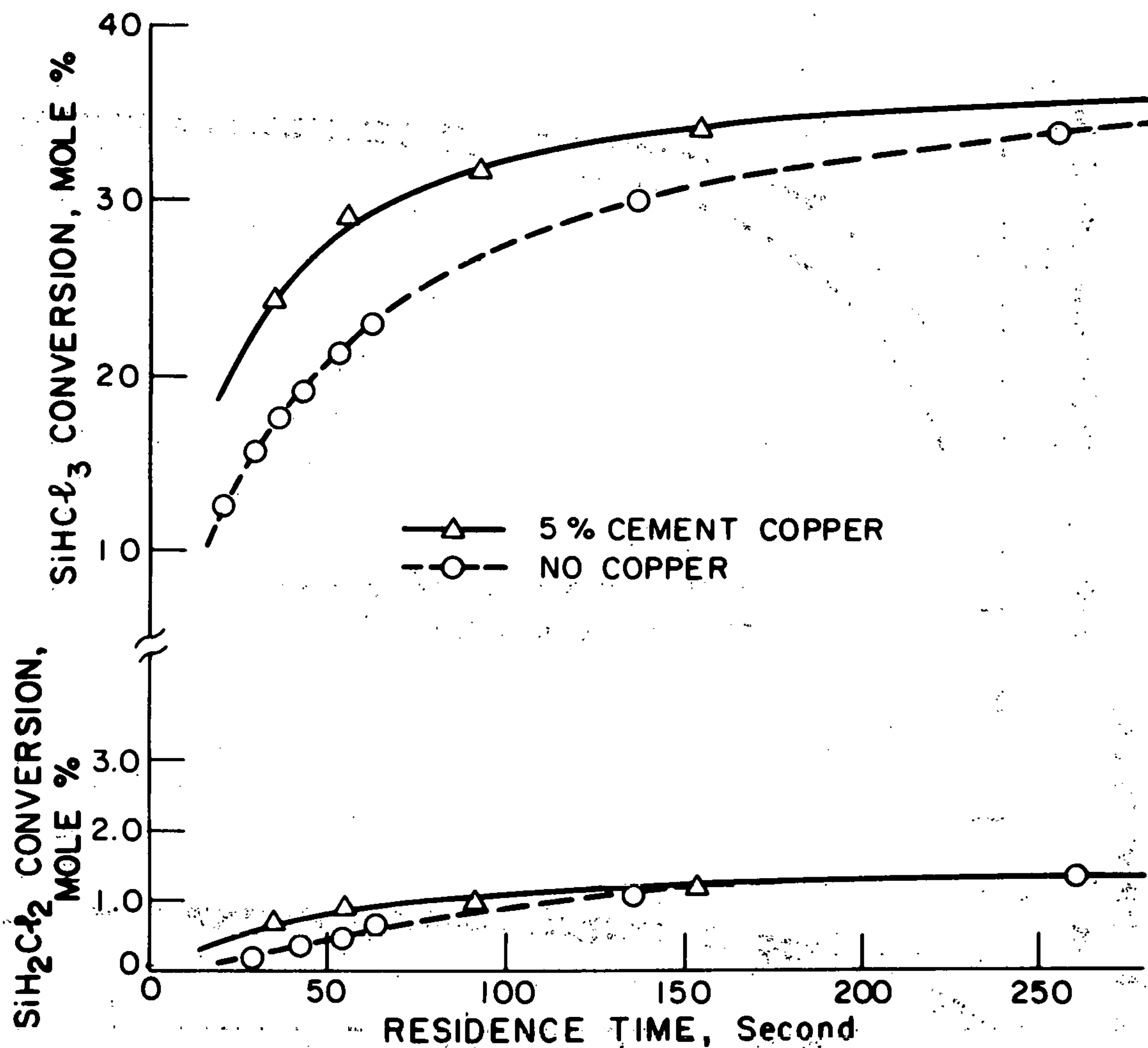


FIGURE XI HYDROCHLORINATION OF $SiC\ell_4$ AT 500 PSIG, 450°C AND $H_2/SiC\ell_4 = 2.8$ WITH AND WITHOUT COPPER CATALYST

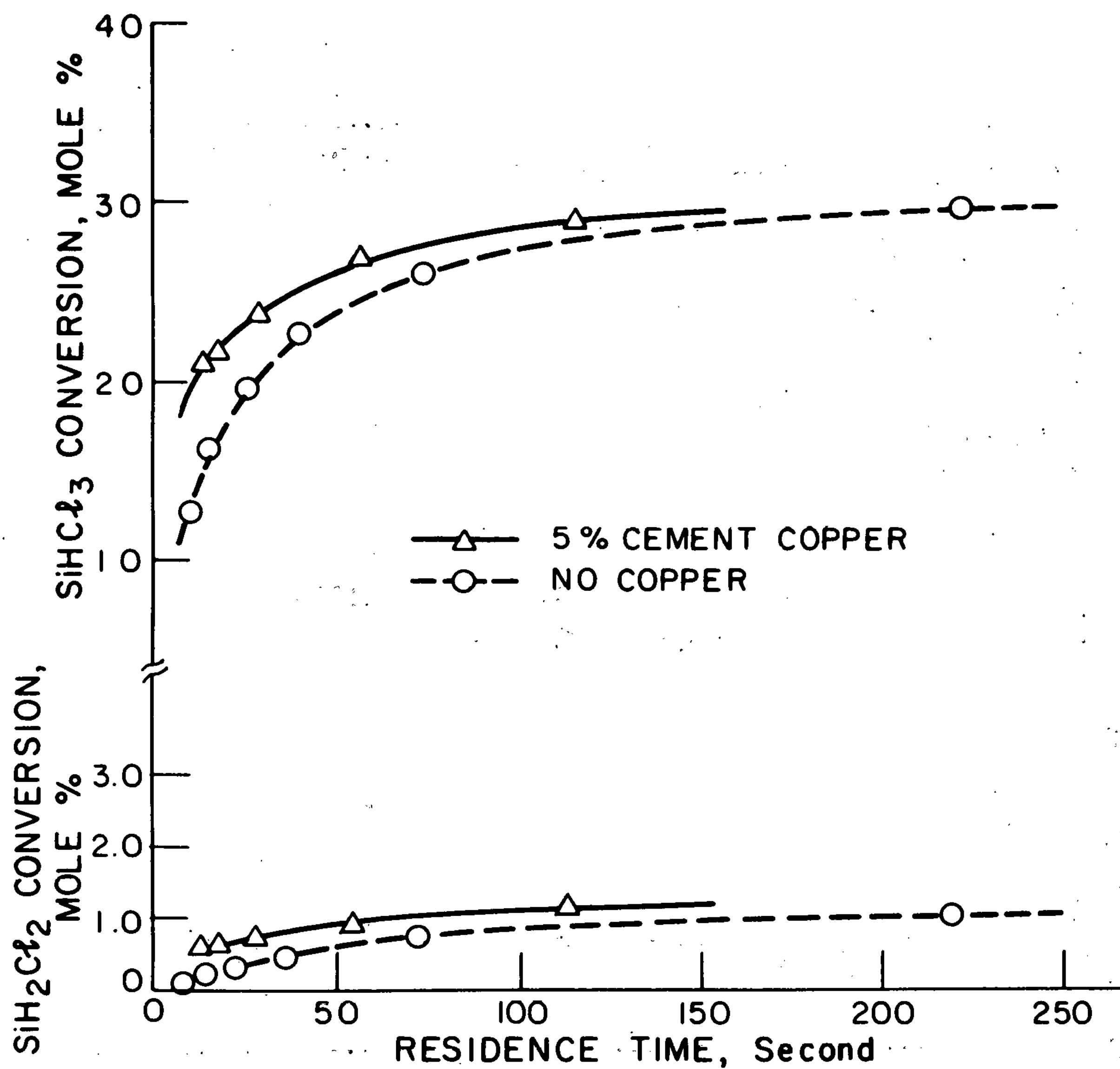


FIGURE XII HYDROCHLORINATION OF $SiC\ell_4$ AT 300 PSIG, 500°C AND $H_2/SiC\ell_4$ = 1.0 WITH AND WITHOUT COPPER CATALYST

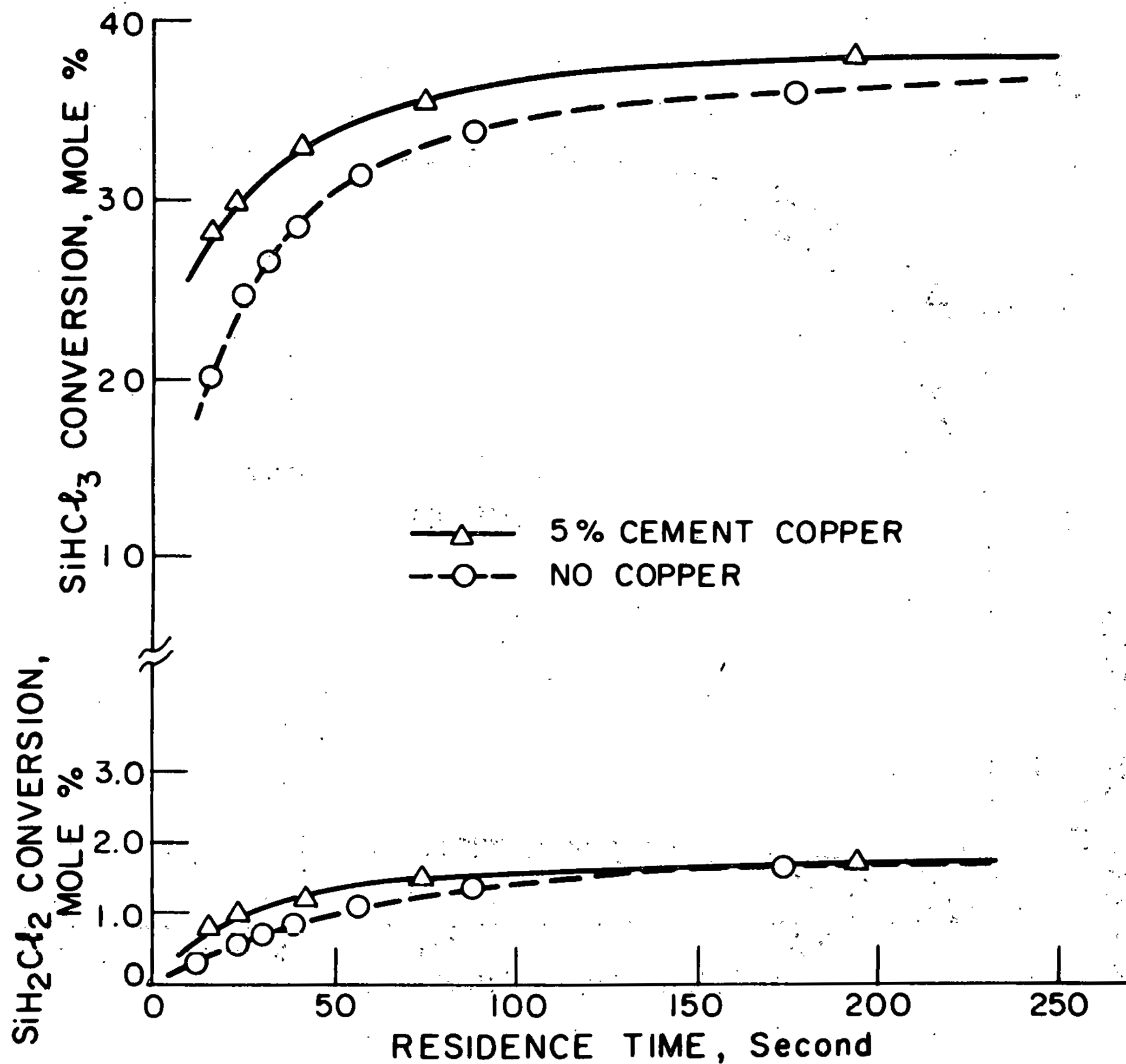


FIGURE XIII HYDROCHLORINATION OF $SiCl_4$ AT 300 PSIG, 500°C AND $H_2/SiCl_4$=2.8 WITH AND WITHOUT COPPER CATALYST

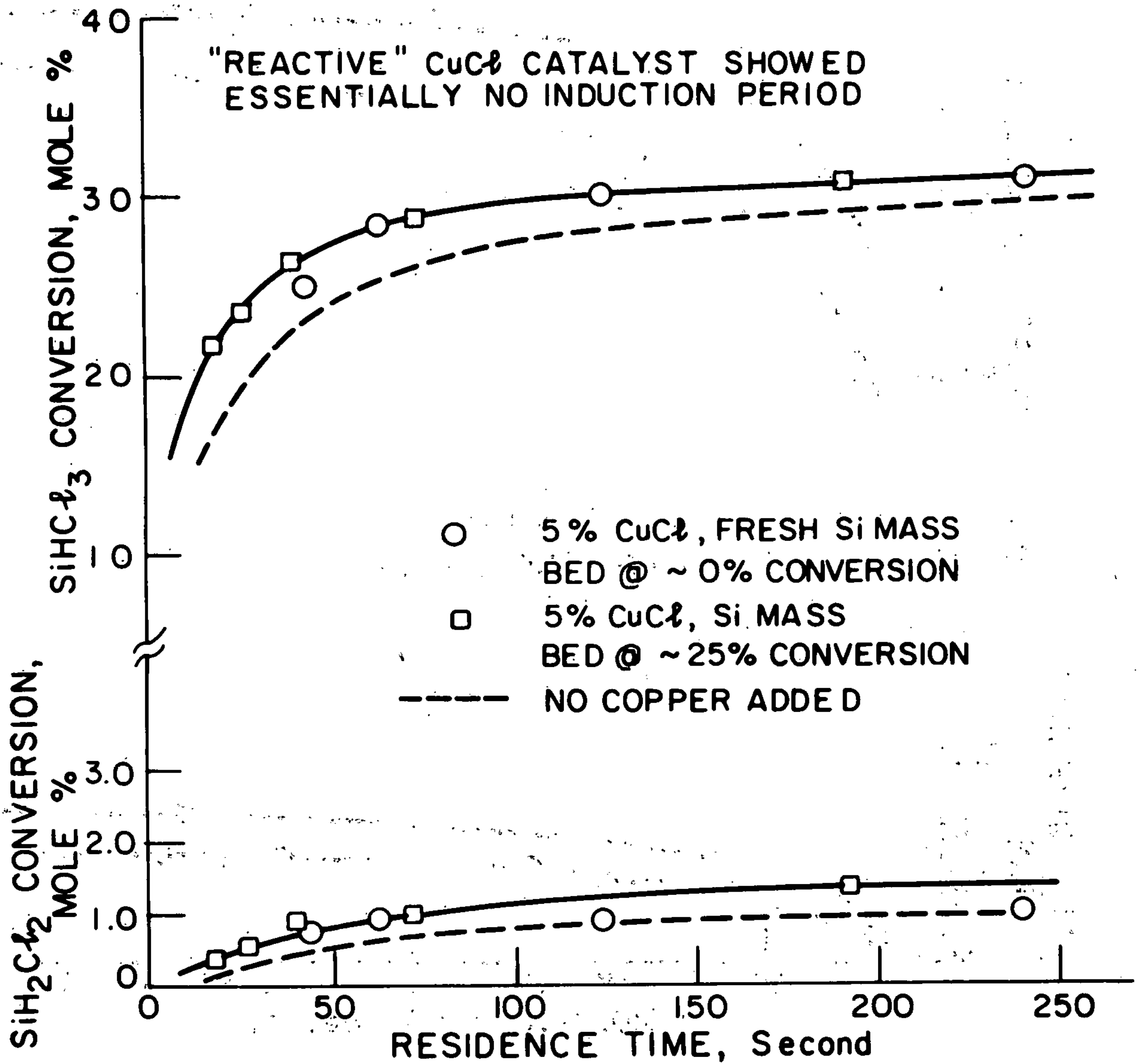


FIGURE XIV HYDROCHLORINATION OF $SiCl_4$ AT 300 PSIG, 500°C AND $H_2/SiCl_4$ = 1.0 WITH 5% CuCℓ CATALYST

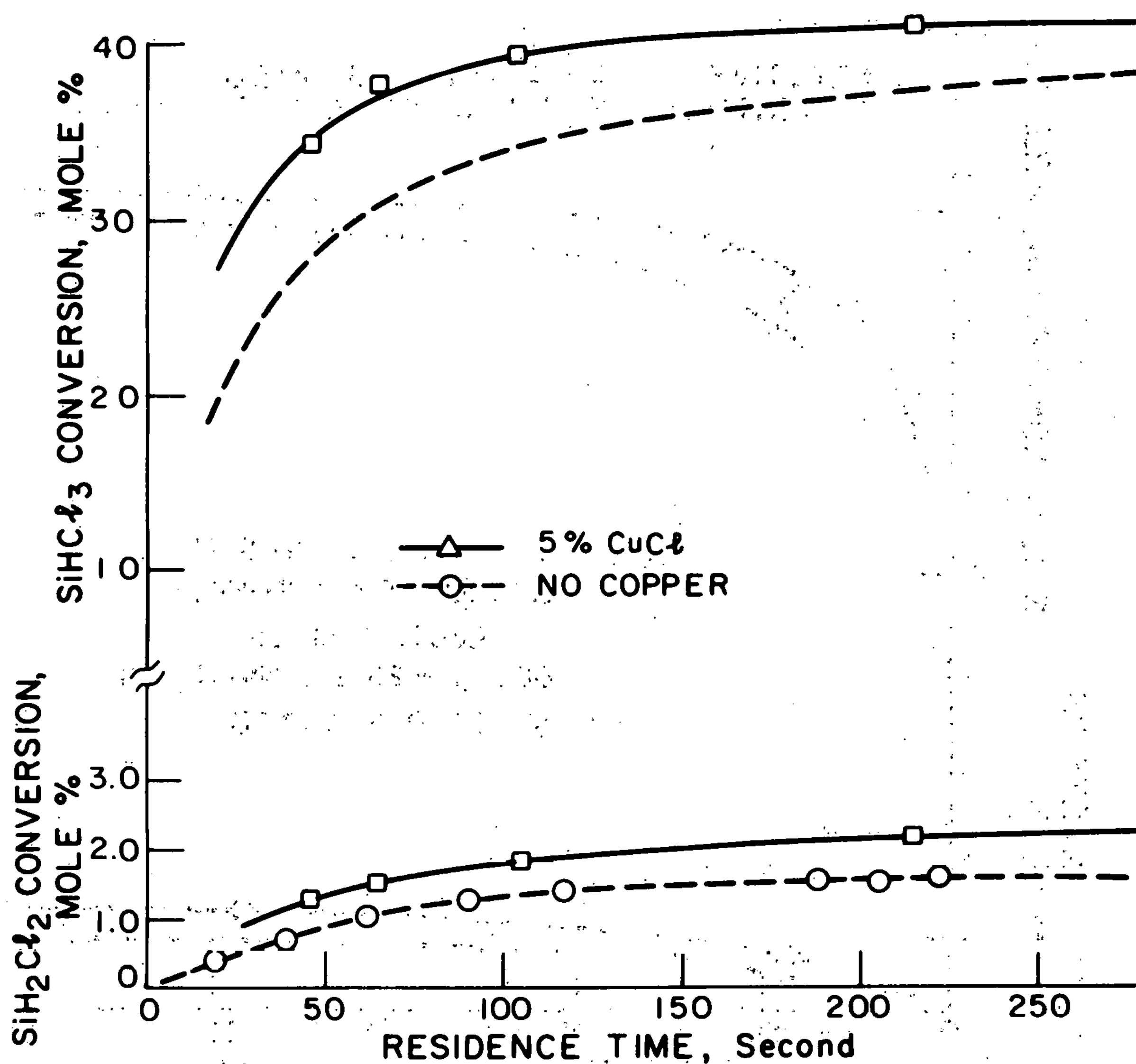


FIGURE XV HYDROCHLORINATION OF $SiCl_4$ AT 500 PSIG, 500°C AND $H_2/SiCl_4$ = 2.8 WITH AND WITHOUT COPPER CATALYST

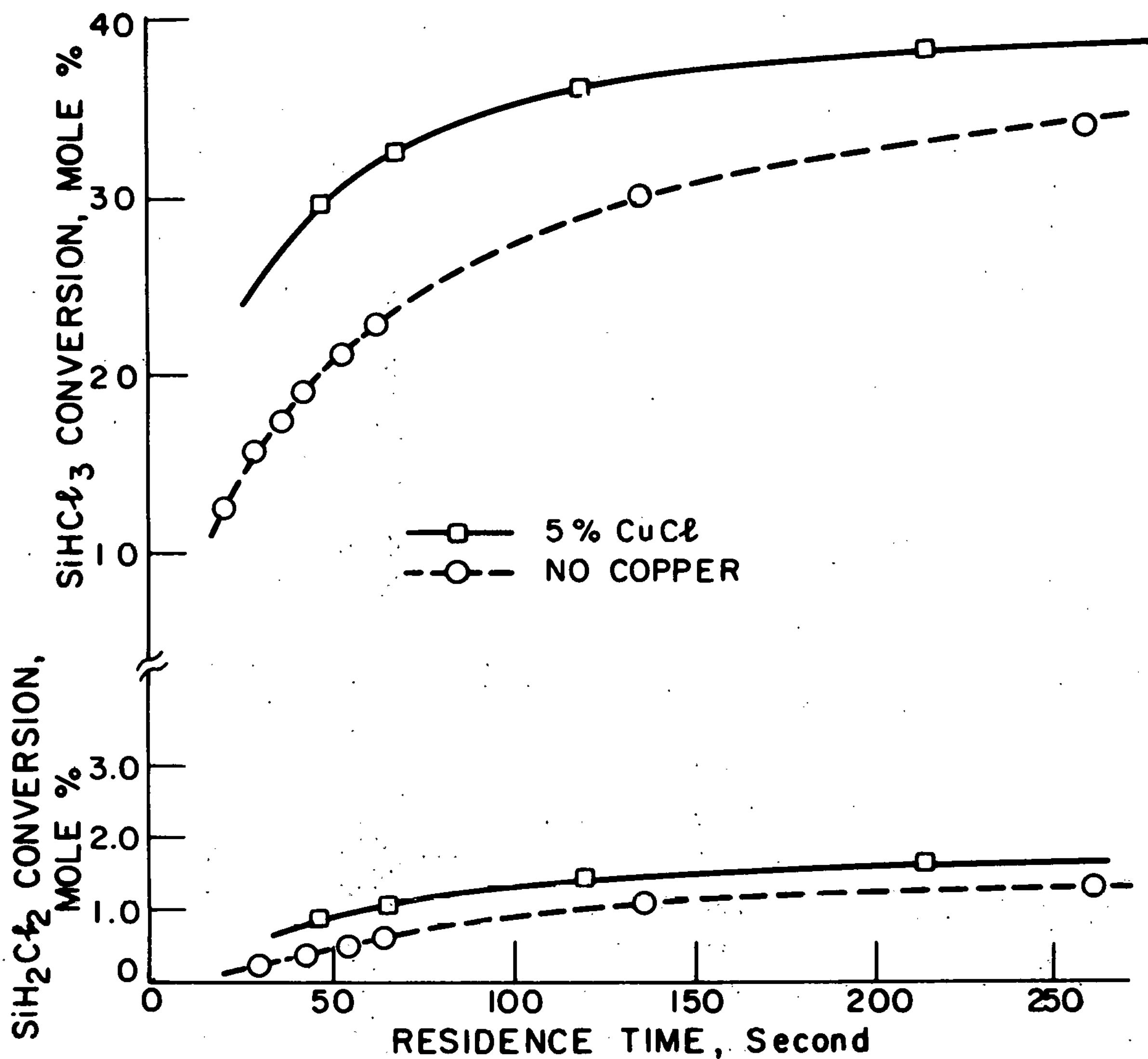


FIGURE XVI HYDROCHLORINATION OF $SiCl_4$ AT 500 PSIG, 450°C AND $H_2/SiCl_4$=2.8 WITH AND WITHOUT COPPER CATALYST

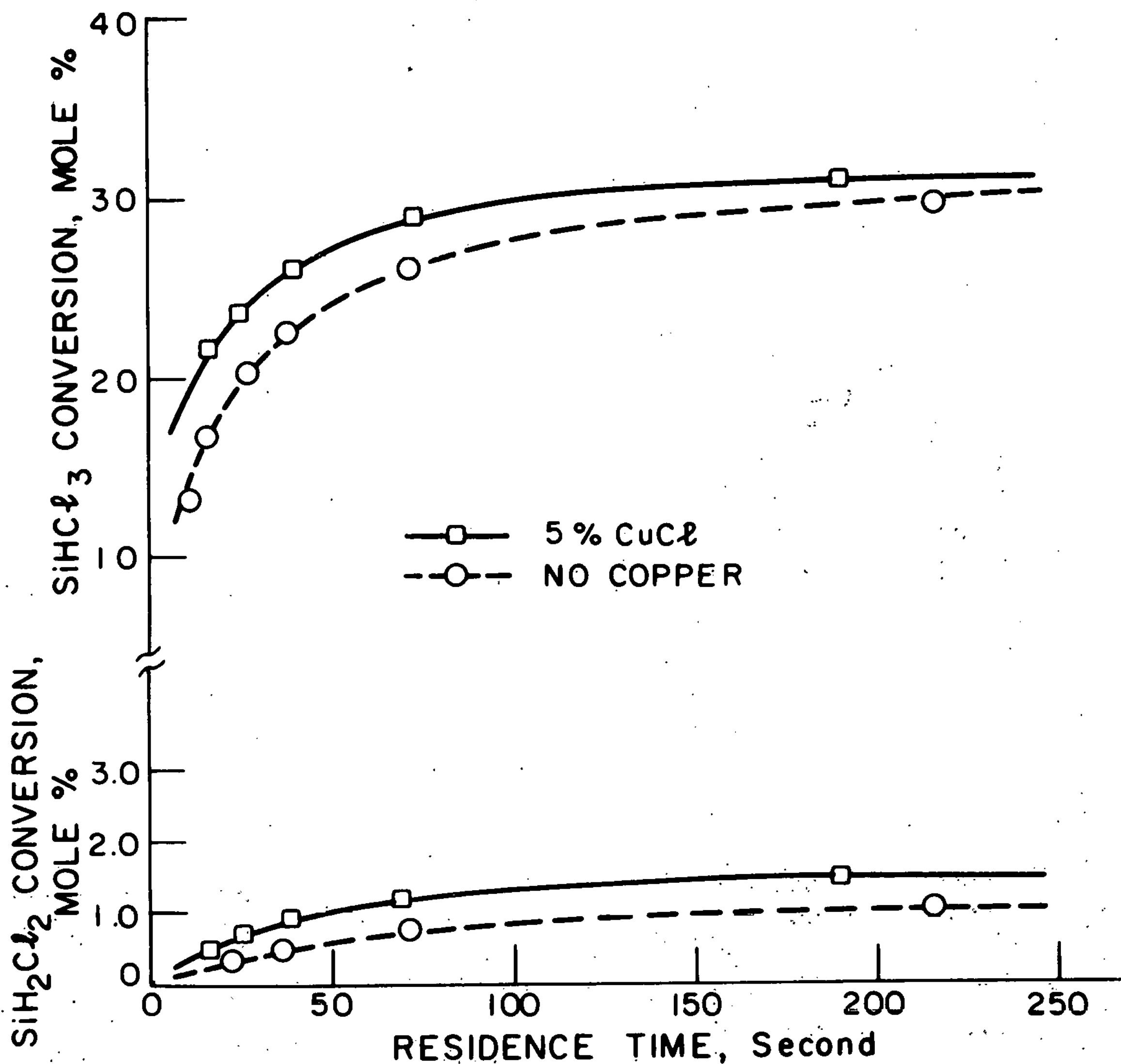


FIGURE XVII HYDROCHLORINATION OF $SiCl_4$ AT 300 PSIG, 500°C AND $H_2/SiCl_4$ = 1.0 WITH AND WITHOUT COPPER CATALYST

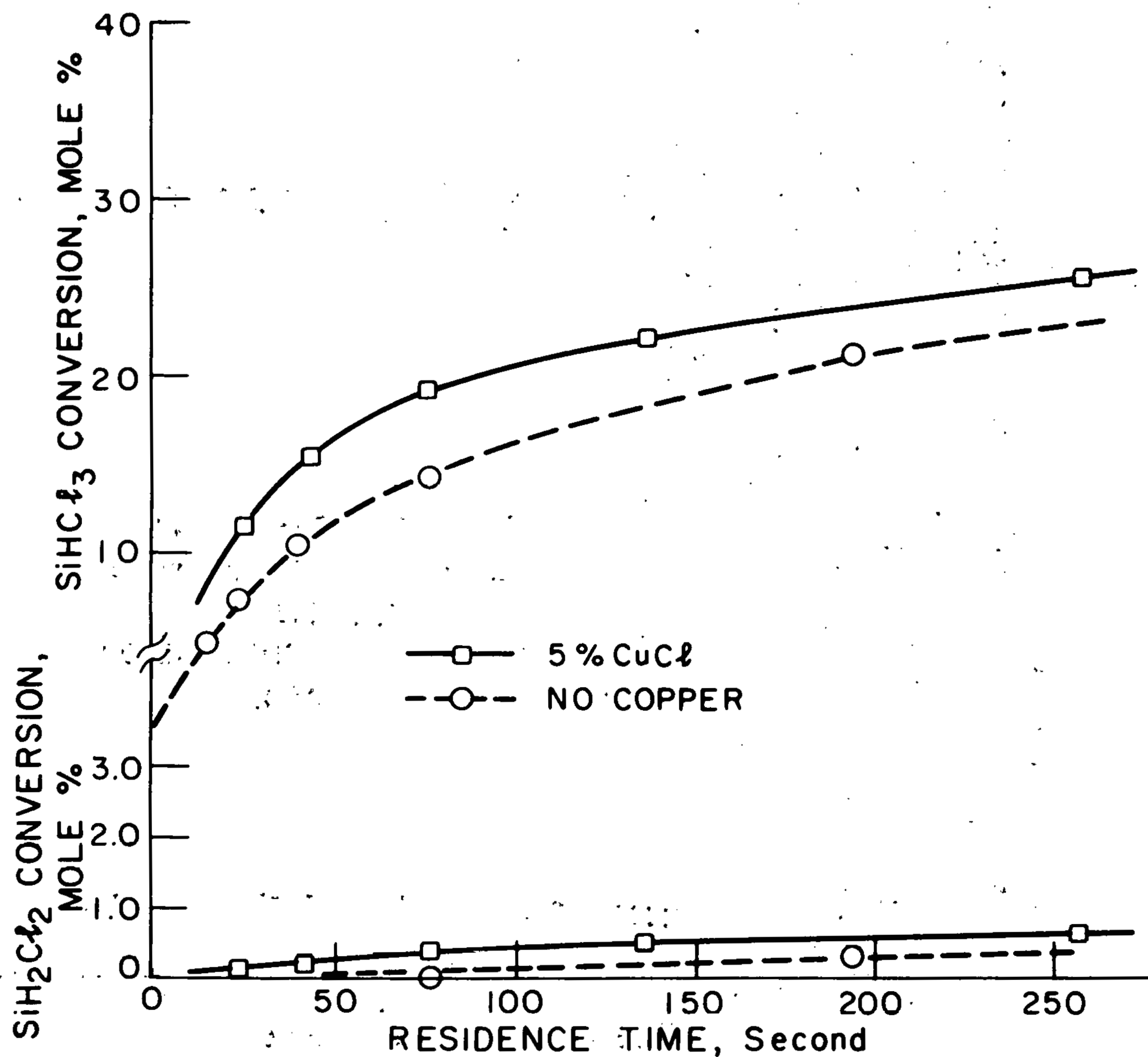


FIGURE XVIII HYDROCHLORINATION OF $SiC\ell_4$ AT 300 PSIG, 400°C AND $H_2/SiC\ell_4$ = 1.0 WITH AND WITHOUT COPPER CATALYST

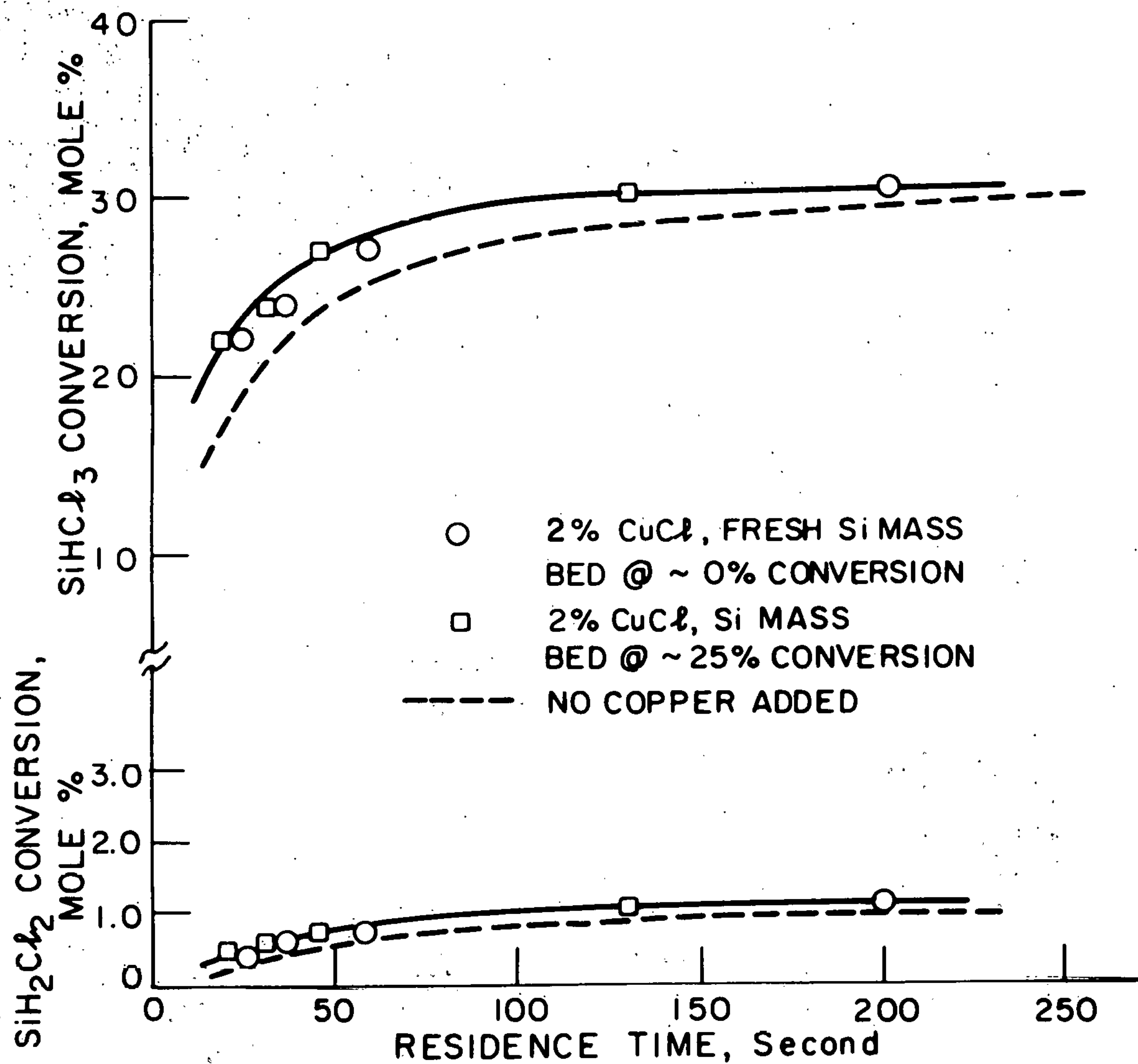


FIGURE XIX HYDROCHLORINATION OF $SiC\ell_4$ AT 300 PSIG, 500°C AND $H_2/SiC\ell_4$ = 1.0 WITH 2% CuCℓ INITIALLY ADDED

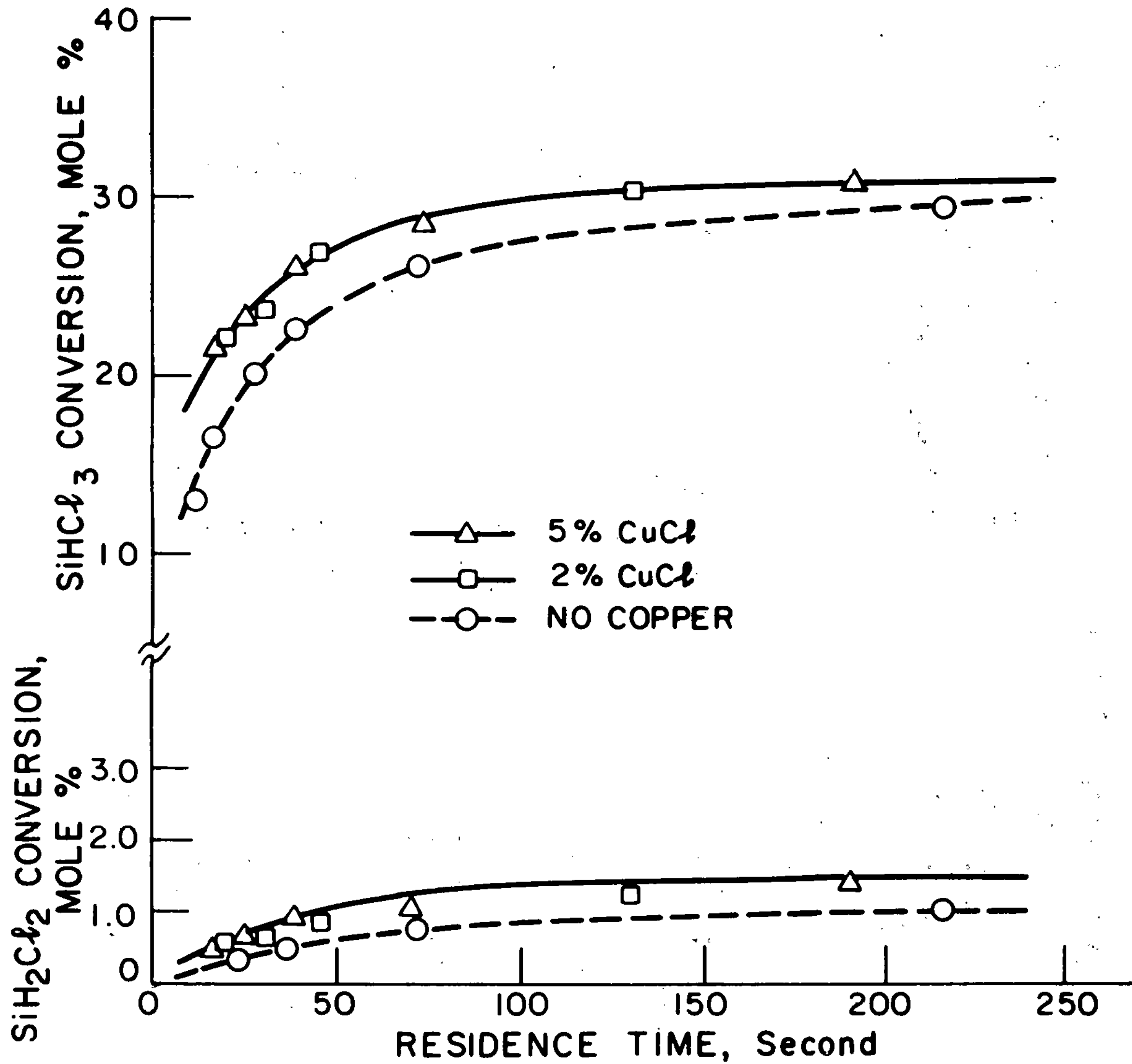


FIGURE XX HYDROCHLORINATION OF $SiCl_4$ AT 300 PSIG, 500°C AND $H_2/SiCl_4$ = 1.0 WITH 2% AND 5% CuCl CATALYST

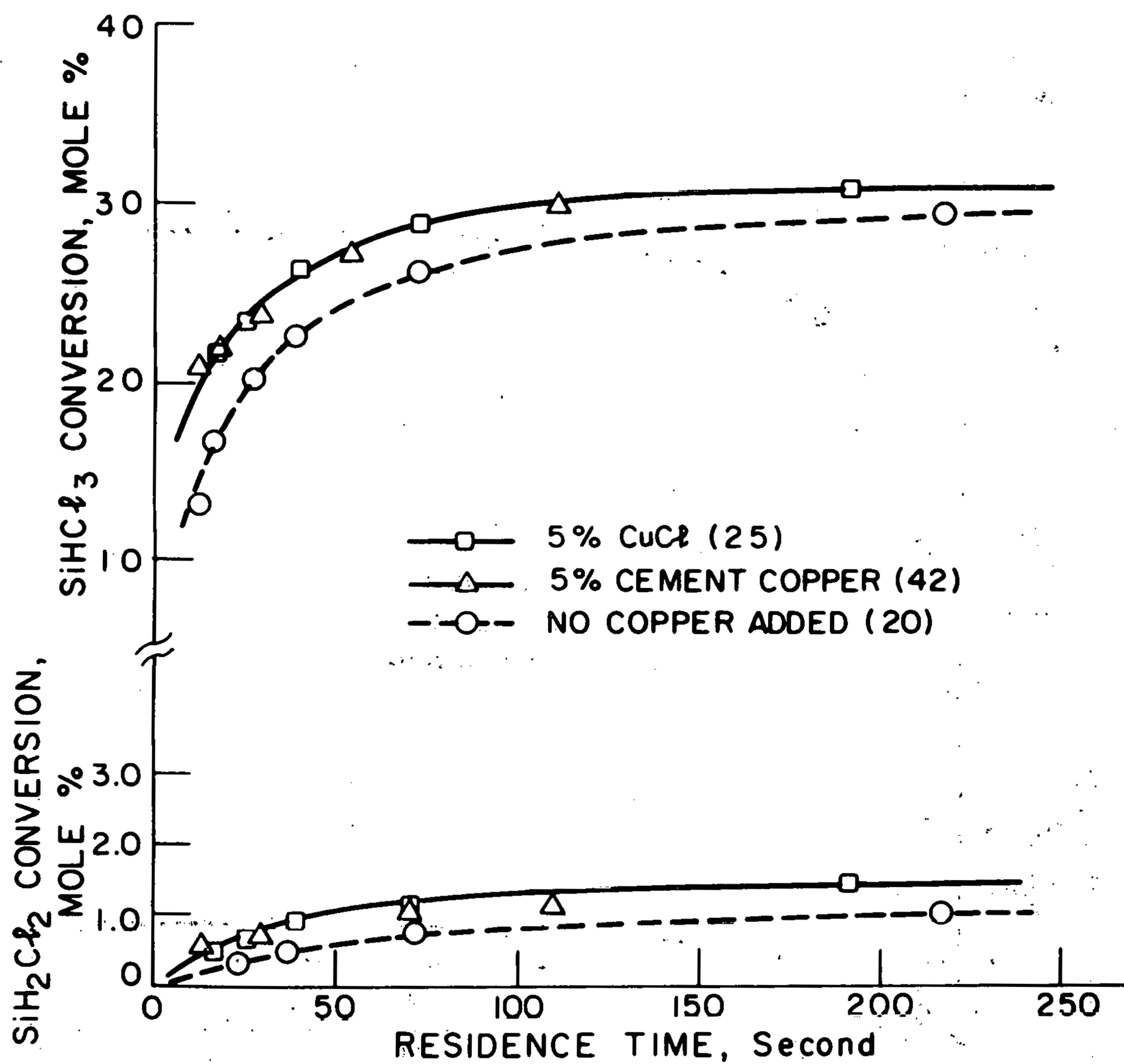


FIGURE XXI HYDROCHLORINATION OF $SiCl_4$ AT 300 PSIG, 500°C AND $H_2/SiCl_4$ = 1.0 WITH AND WITHOUT COPPER CATALYST

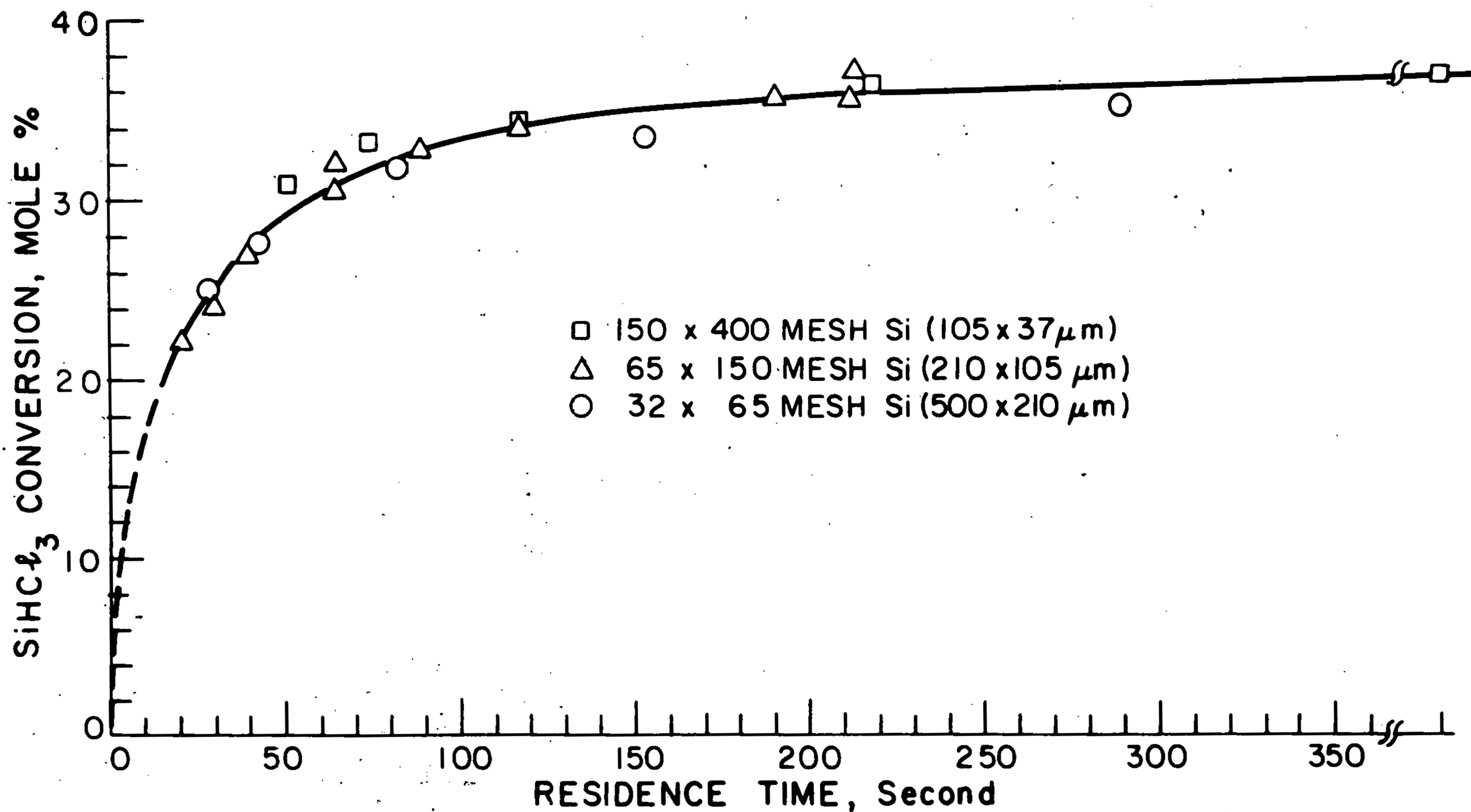


FIGURE XXII PARTICLE SIZE DISTRIBUTION STUDIES: THE HYDROCHLORINATION OF $SiCl_4$ AND M. G. Si AT 500°C AND $H_2/SiCl_4$ RATIO OF 2.8

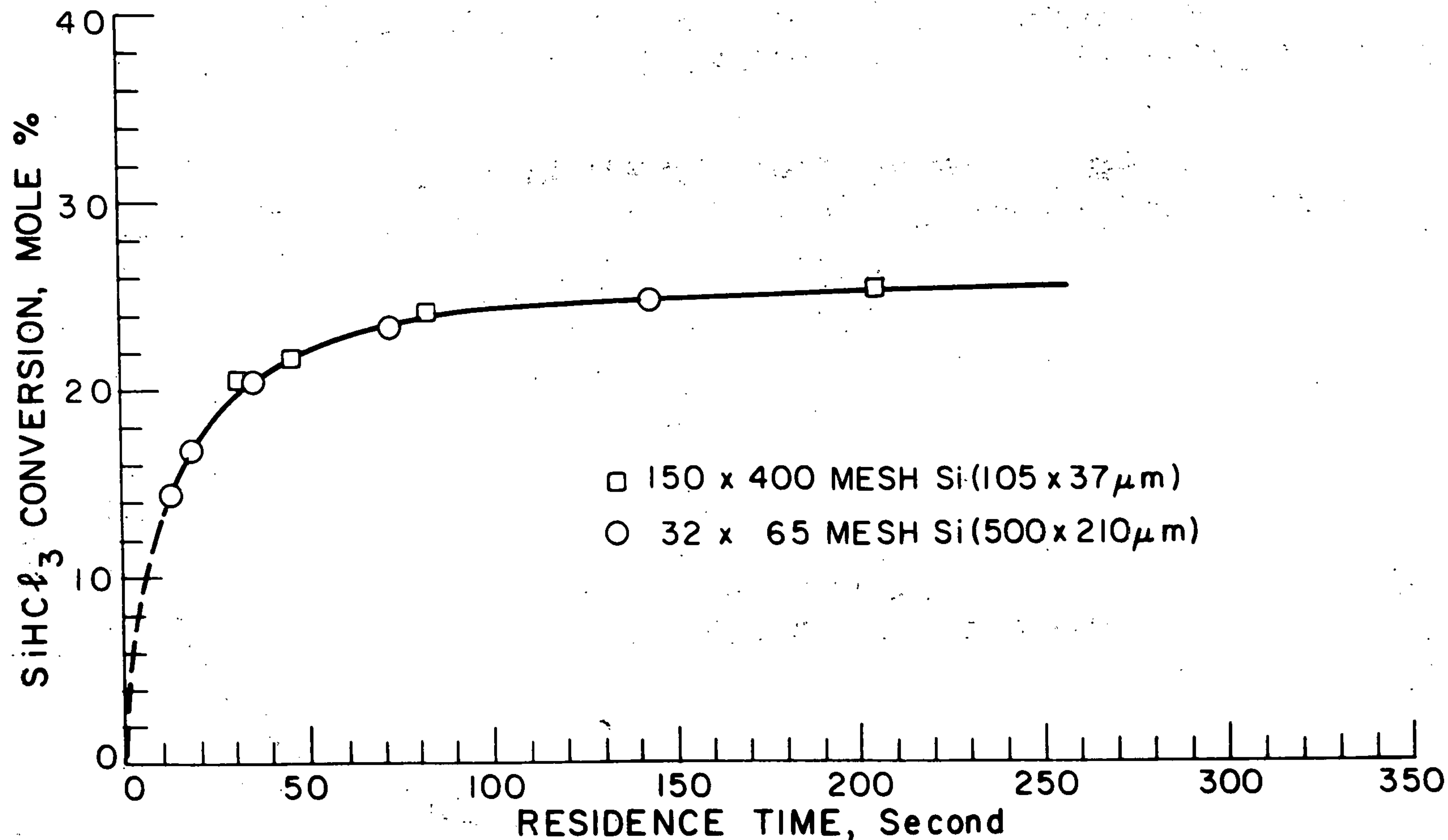


FIGURE XXIII PARTICLE SIZE DISTRIBUTION STUDIES: THE HYDROCHLORINATION OF $SiC\ell_4$ AND M.G. Si AT 300 PSIG, 500°C AND $H_2/SiC\ell_4$ RATIO OF 1.0

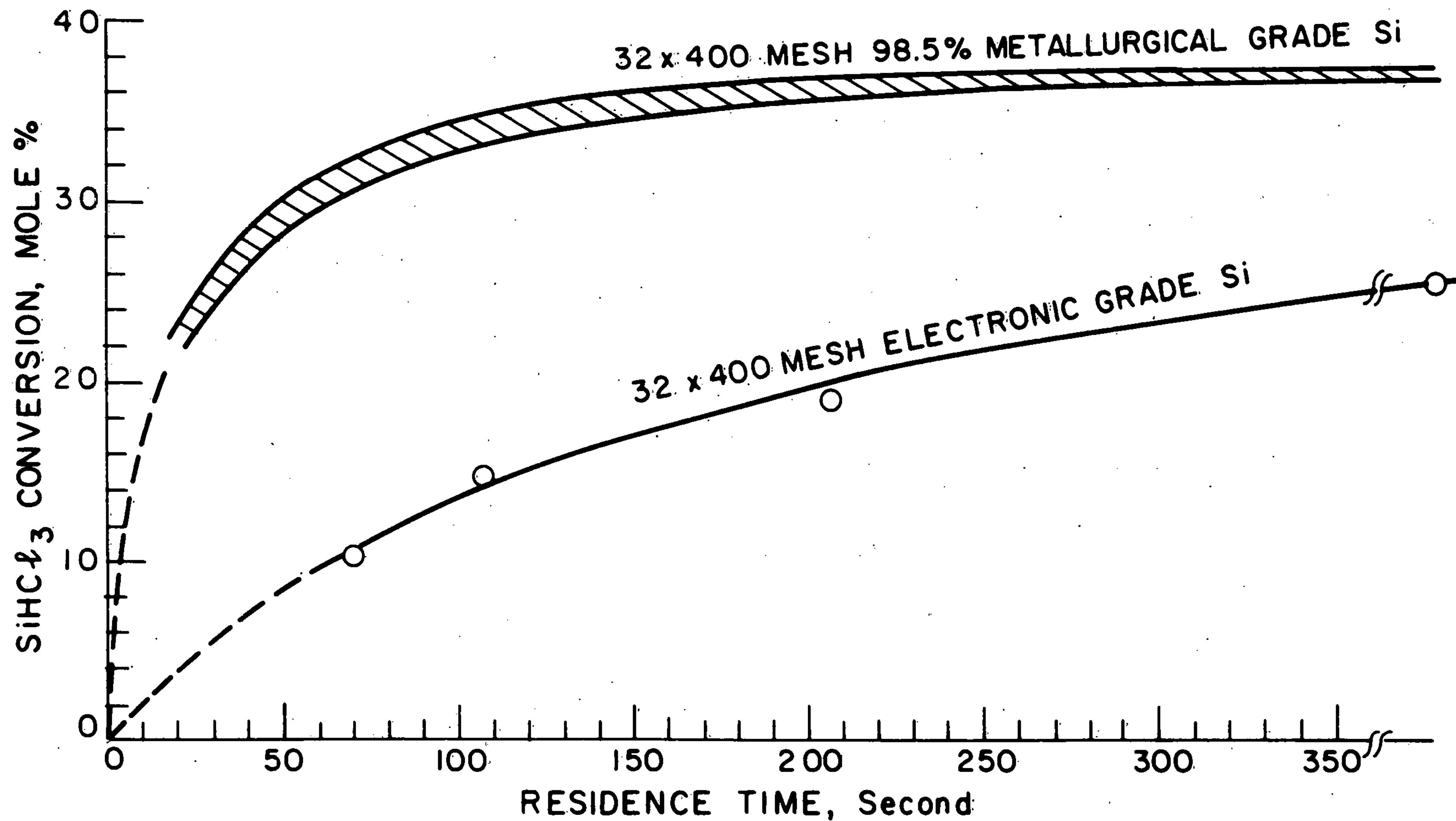


FIGURE XXIV HYDROCHLORINATION OF $SiCl_4$ TO $SiHCl_3$ AND Si AT 500 PSIG, 500°C AND $H_2/SiCl_4 = 2.8$

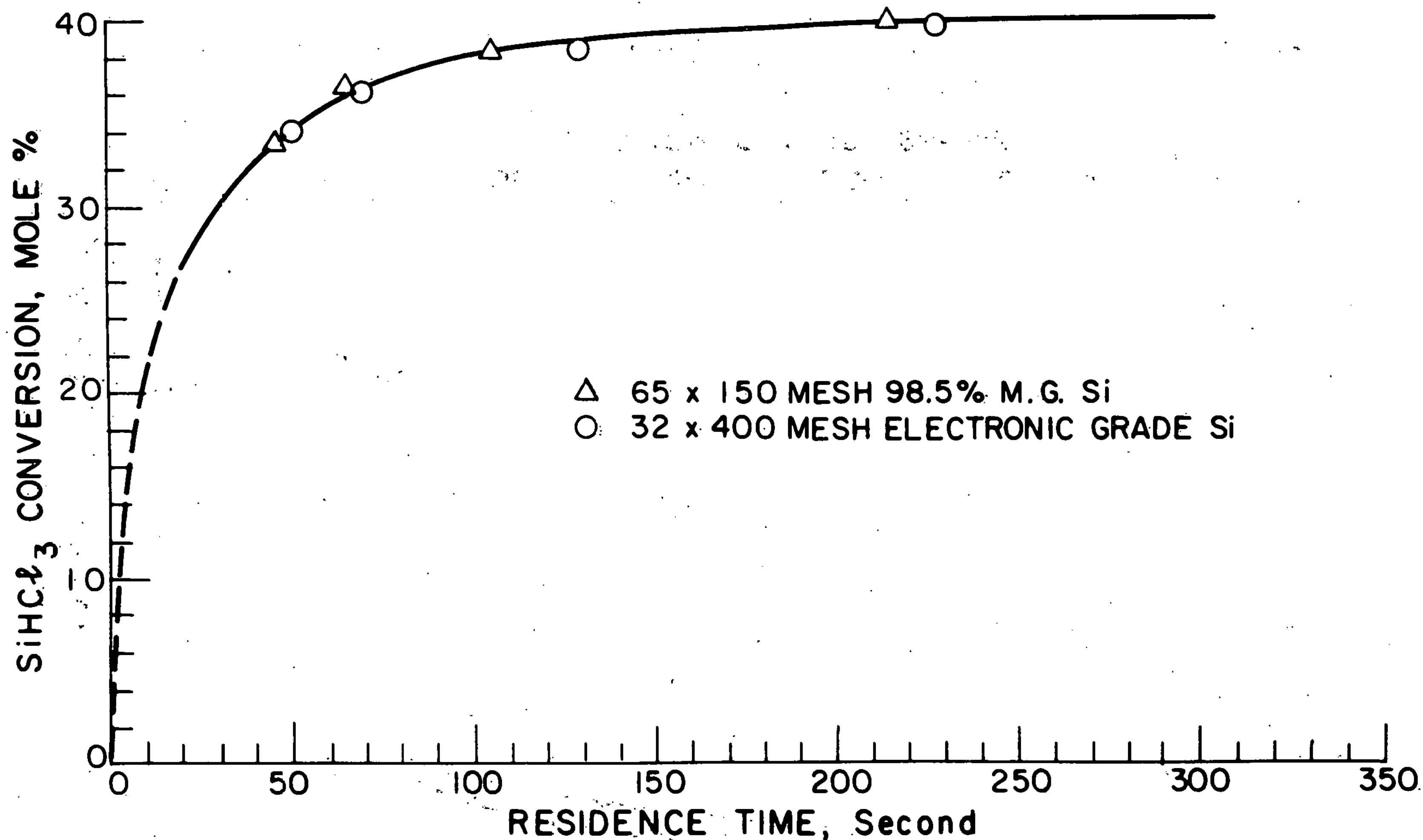


FIGURE XXV HYDROCHLORINATION OF $SiC\ell_4$ TO $SiHC\ell_3$ AND Si AT 500 PSIG, 500°C AND $H_2/SiC\ell_4$ = 2.8 WITH 5% CUPROUS CHLORIDE CATALYST

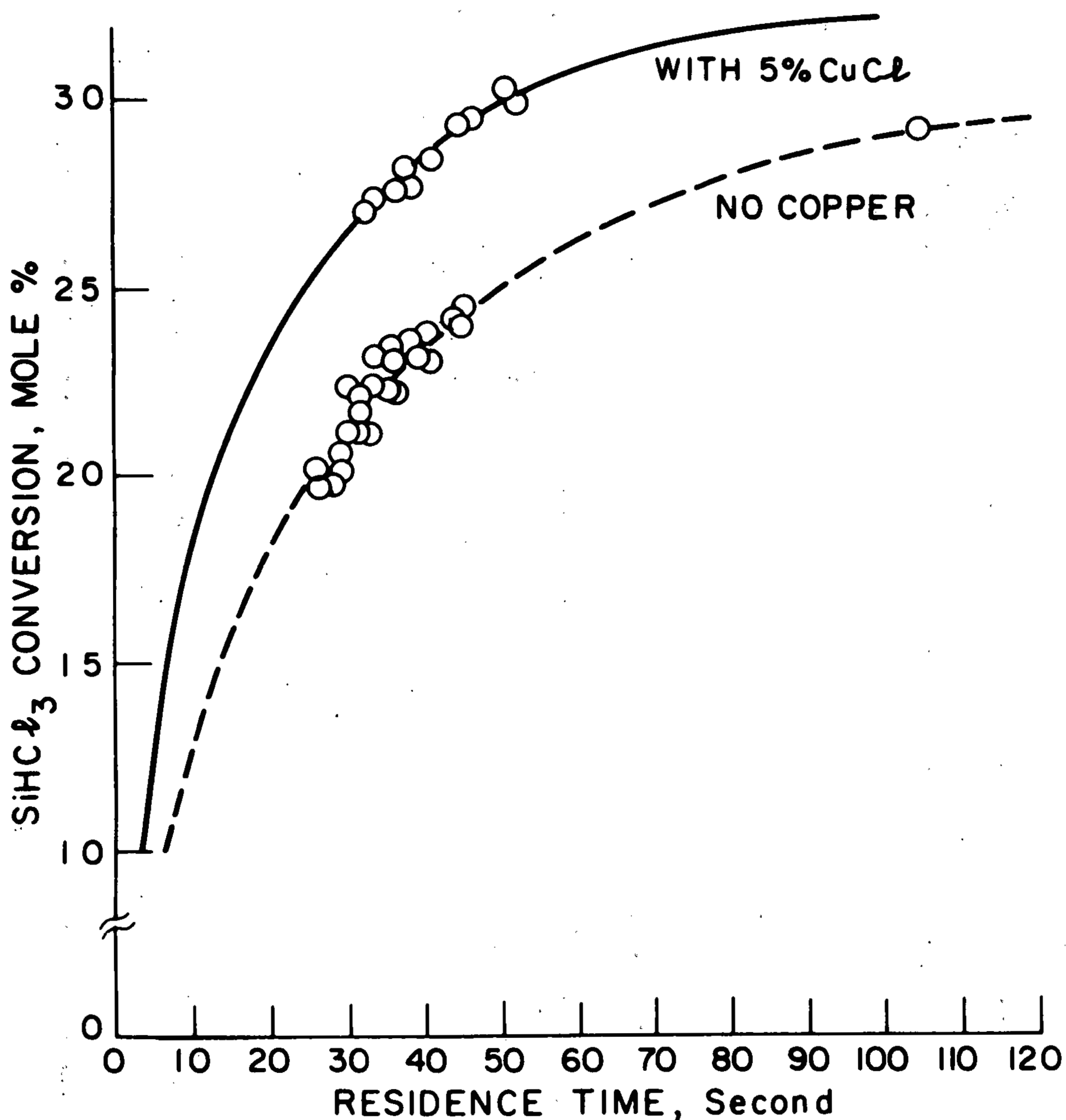


FIGURE XXVI PROLONGED REACTION OF $SiCl_4$ AND M.G. SILICON AT 500°C, 300 PSIG, $H_2/SiCl_4 = 2.0$ WITH AND WITHOUT COPPER ADDED

FIGURE XXVII

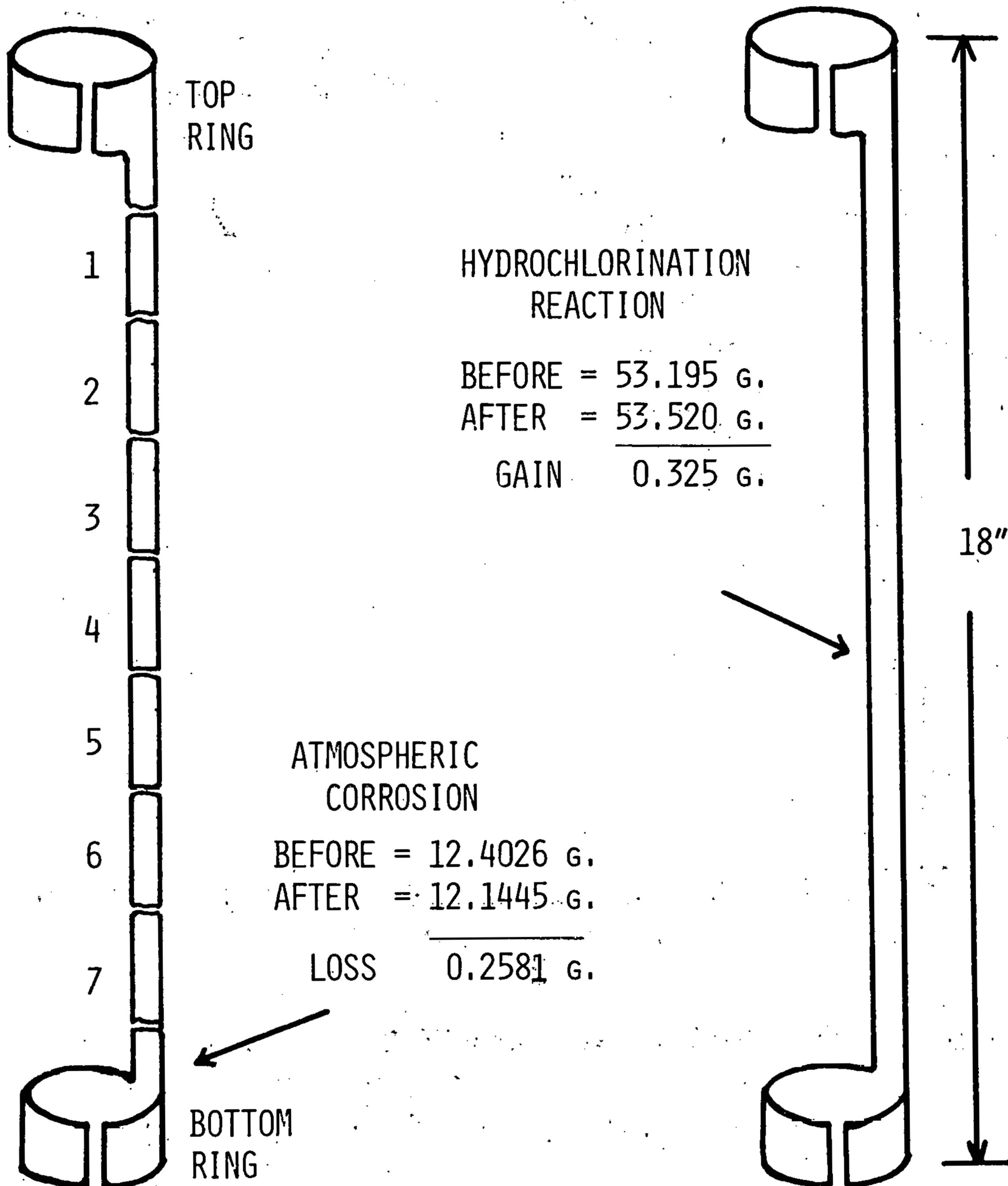
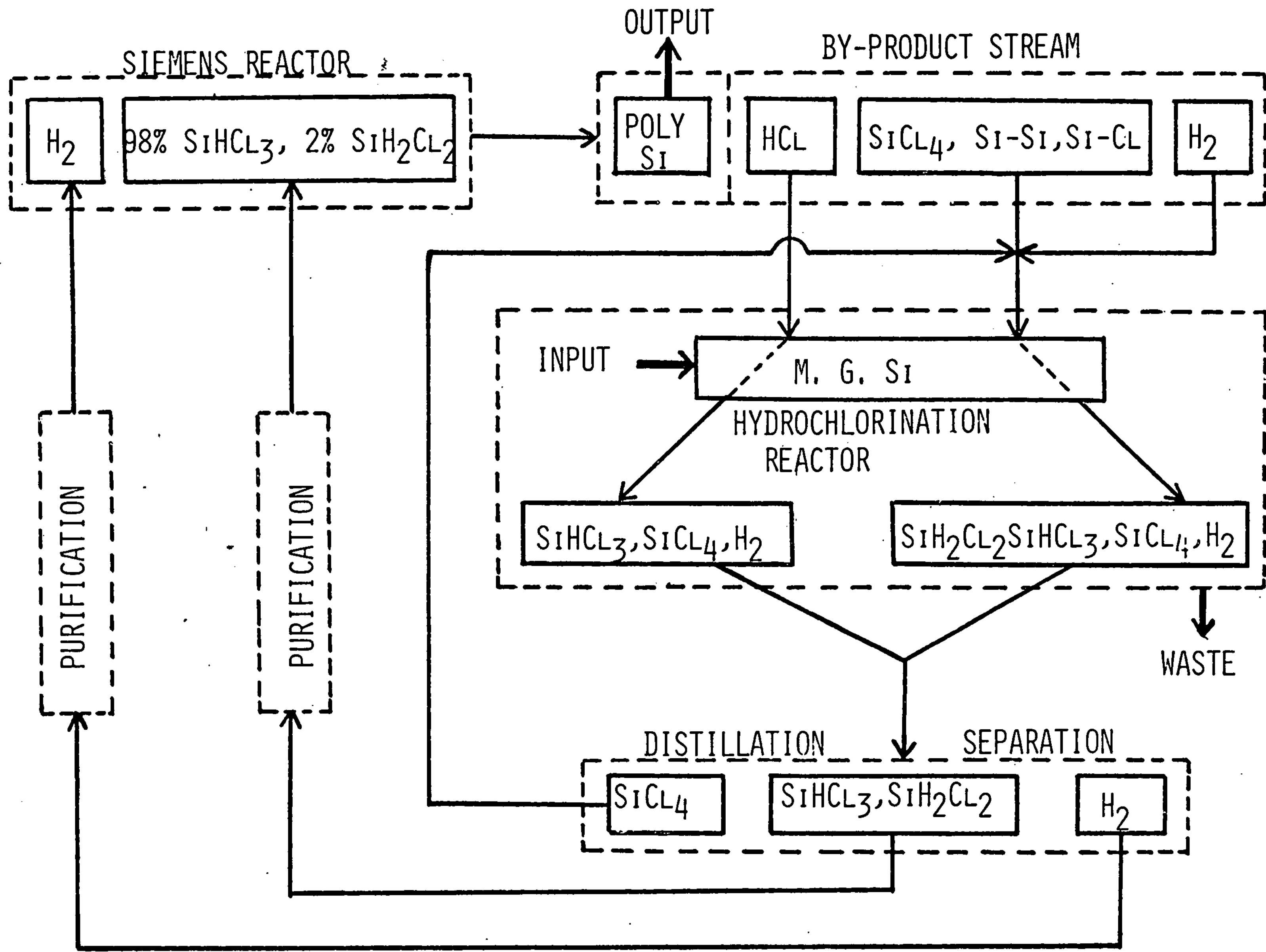


FIGURE XXVIII CLOSED-LOOP SIEMENS PROCESS



*U.S. GOVERNMENT PRINTING OFFICE: 1981-740-145/2258