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Covering the period March 31, 1979-April 1, 1981
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INVESTIGATION OF
THE HYDROGENATION
OF SiCl₄
JPL Contract No. 955 382

Low-Cost Solar Array Project
Silicon Material Task
to
Jet Propulsion Laboratory
California Institute of Technology

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LOW-COST SOLAR ARRAY PROJECT

SILICON MATERIAL TASK

"Investigation of the Hydrogenation of SiCl₄"

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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,

\[ 3 \text{SiCl}_4 + 2\text{H}_2 + \text{Si} \rightleftharpoons 4 \text{SiHCl}_3 \]

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

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reaction at pressures up to 500 psig. Reaction kinetic measurements were carried out as a function of reactor pressure, reaction temperature and \( \text{H}_2/\text{SiCl}_4 \) 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 latitude 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

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 H2/SiCl4 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
VI. REFERENCES

VII. APPENDICES

TABLE I, HYDROCHLORINATION OF SiC\textsubscript{14} AND M.G. SILICON AT 500 PSIG, 500°C, H\textsubscript{2}/SiCl\textsubscript{4} = 2.8

TABLE II, HYDROCHLORINATION OF SiC\textsubscript{14} AND M.G. SILICON AT 500 PSIG, 450°C, H\textsubscript{2}/SiCl\textsubscript{4} = 2.8

TABLE III, HYDROCHLORINATION OF SiC\textsubscript{14} AND M.G. SILICON AT 500 PSIG, 550°C, H\textsubscript{2}/SiCl\textsubscript{4} = 2.8

TABLE IV, HYDROCHLORINATION OF SiC\textsubscript{14} AND M.G. SILICON AT 300 PSIG, 500°C, H\textsubscript{2}/SiCl\textsubscript{4} = 1.0

TABLE V, HYDROCHLORINATION OF SiC\textsubscript{14} AND M.G. SILICON AT 300 PSIG, 450°C, H\textsubscript{2}/SiCl\textsubscript{4} = 1.0

TABLE VI, HYDROCHLORINATION OF SiC\textsubscript{14} AND M.G. SILICON AT 300 PSIG, 450°C, H\textsubscript{2}/SiCl\textsubscript{4} = 1.0

TABLE VII, HYDROCHLORINATION OF SiC\textsubscript{14} AND M.G. SILICON AT 300 PSIG, 400°C, H\textsubscript{2}/SiCl\textsubscript{4} = 1.0

TABLE VIII, HYDROCHLORINATION OF SiC\textsubscript{14} AND M.G. SILICON AT 300 PSIG, 500°C, H\textsubscript{2}/SiCl\textsubscript{4} = 2.8

TABLE IX, HYDROCHLORINATION OF SiC\textsubscript{14} AND M.G. SILICON AT 300 PSIG, 450°C, H\textsubscript{2}/SiCl\textsubscript{4} = 2.8

TABLE X, HYDROCHLORINATION OF SiC\textsubscript{14} AND M.G. SILICON AT 300 PSIG, 400°C, H\textsubscript{2}/SiCl\textsubscript{4} = 2.8

TABLE XI, HYDROCHLORINATION OF SiC\textsubscript{14} AND M.G. SILICON AT 500 PSIG, 500°C AND H\textsubscript{2}/SiCl\textsubscript{4} RATIO OF 2.8 WITH 5% CEMENT COPPER

TABLE XII, HYDROCHLORINATION OF SiC\textsubscript{14} AND M.G. SILICON AT 500 PSIG, 450°C AND H\textsubscript{2}/SiCl\textsubscript{4} RATIO OF 2.8 WITH 5% CEMENT COPPER

TABLE XIII, HYDROCHLORINATION OF SiC\textsubscript{14} AND M.G. SILICON AT 300 PSIG, 500°C AND H\textsubscript{2}/SiCl\textsubscript{4} RATIO OF 1.0 WITH 5% CEMENT COPPER

TABLE XIV, HYDROCHLORINATION OF SiC\textsubscript{14} AND M.G. SILICON AT 300 PSIG, 500°C AND H\textsubscript{2}/SiCl\textsubscript{4} RATIO OF 2.8 WITH 5% CEMENT COPPER

TABLE XV, HYDROCHLORINATION OF SiC\textsubscript{14} AND M.G. SILICON AT 500 PSIG, 500°C AND H\textsubscript{2}/SiCl\textsubscript{4} RATIO OF 2.8 WITH 5% CUPROUS CHLORIDE
TABLE XVI, HYDROCHLORINATION OF SiC\textsubscript{14} AND M.G. SILICON AT 500 PSIG, 450\textdegree C AND H\textsubscript{2}/SiC\textsubscript{14} RATIO OF 2.8 WITH 5\% CUPROUS CHLORIDE

TABLE XVII, HYDROCHLORINATION OF SiC\textsubscript{14} AND M.G. SILICON AT 300 PSIG, 500\textdegree C AND H\textsubscript{2}/SiC\textsubscript{14} RATIO OF 1.0 WITH 5\% CUPROUS CHLORIDE

TABLE XVIII, HYDROCHLORINATION OF SiC\textsubscript{14} AND M.G. SILICON AT 300 PSIG, 400\textdegree C AND H\textsubscript{2}/SiC\textsubscript{14} RATIO OF 1.0 WITH 5\% CUPROUS CHLORIDE

TABLE XIX, HYDROCHLORINATION OF SiC\textsubscript{14} AND M.G. SILICON AT 300 PSIG, 500\textdegree C AND H\textsubscript{2}/SiC\textsubscript{14} 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 SiC\textsubscript{14} AND 32 x 65 MESH M.G. SILICON AT 500 PSIG, 500\textdegree C AND H\textsubscript{2}/SiC\textsubscript{14} = 2.8

TABLE XXII, HYDROCHLORINATION OF SiC\textsubscript{14} AND 150 x 400 MESH M.G. SILICON AT 500 PSIG, 500\textdegree C AND H\textsubscript{2}/SiC\textsubscript{14} = 2.8

TABLE XXIII, HYDROCHLORINATION OF SiC\textsubscript{14} AND 150 x 400 MESH M.G. SILICON AT 300 PSIG, 500\textdegree C AND H\textsubscript{2}/SiC\textsubscript{14} = 1.0

TABLE XXIV, HYDROCHLORINATION OF SiC\textsubscript{14} AND 32 x 65 MESH M.G. SILICON AT 300 PSIG, 500\textdegree C AND H\textsubscript{2}/SiC\textsubscript{14} = 1.0

TABLE XXV, HYDROCHLORINATION OF SiC\textsubscript{14} AND ELECTRONIC GRADE SILICON AT 500 PSIG, 500\textdegree C AND H\textsubscript{2}/SiC\textsubscript{14} RATIO OF 2.8

TABLE XXVI, HYDROCHLORINATION OF SiC\textsubscript{14} AND ELECTRONIC GRADE SILICON AT 500 PSIG, 500\textdegree C AND H\textsubscript{2}/SiC\textsubscript{14} RATIO OF 2.8 WITH 5\% CuCl ADDED

TABLE XXVII, SELECTED KINETIC DATA FROM A PROLONGED HYDROCHLORINATION REACTION AT 300 PSIG, 500\textdegree C AND H\textsubscript{2}/SiC\textsubscript{14} RATIO OF 2.0

FIGURE I, THE HYDROCHLORINATION APPARATUS

FIGURE II, H\textsubscript{2}/SiC\textsubscript{14} FEED INLET TO REACTOR AND GRID DESIGN

FIGURE III, HYDROCHLORINATION REACTION RATE AT 500 PSIG AND H\textsubscript{2}/SiC\textsubscript{14} RATIO OF 2.8 AS A FUNCTION OF TEMPERATURE

FIGURE IV, HYDROCHLORINATION REACTION RATE AT 300 PSIG AND H\textsubscript{2}/SiC\textsubscript{14} RATIO OF 1.0 AS A FUNCTION OF TEMPERATURE
FIGURE V, HYDROCHLORINATION REACTION RATE AT 300 PSIG AND H₂/SiCl₄ RATIO OF 2.8 AS A FUNCTION OF TEMPERATURE

FIGURE VI, HYDROCHLORINATION REACTION RATE AT 300 PSIG AND 500°C AS A FUNCTION OF H₂/SiCl₄ RATIO

FIGURE VII, EFFECT OF REACTOR PRESSURE ON THE HYDROCHLORINATION REACTION RATE AT 450°C AND H₂/SiCl₄ RATIO OF 2.8

FIGURE VIII, EFFECT OF REACTOR PRESSURE ON THE HYDROCHLORINATION REACTION RATE AT 500°C AND H₂/SiCl₄ RATIO OF 2.8

FIGURE IX, HYDROCHLORINATION REACTION RATE AT 300 PSIG, 500°C AND H₂/SiCl₄ = 1.0 WITH 5% CEMENT COPPER AS A FUNCTION OF REACTION TIME

FIGURE X, HYDROCHLORINATION REACTION RATE AT 500 PSIG, 500°C AND H₂/SiCl₄ = 2.8 WITH 5% CEMENT COPPER

FIGURE XI, HYDROCHLORINATION REACTION RATE AT 500 PSIG, 450°C AND H₂/SiCl₄ = 2.8 WITH 5% CEMENT COPPER

FIGURE XII, HYDROCHLORINATION REACTION RATE AT 300 PSIG, 500°C AND H₂/SiCl₄ = 1.0 WITH 5% CEMENT COPPER

FIGURE XIII, HYDROCHLORINATION REACTION RATE AT 300 PSIG, 500°C AND H₂/SiCl₄ = 2.8 WITH 5% CEMENT COPPER

FIGURE XIV, HYDROCHLORINATION REACTION RATE AT 300 PSIG, 500°C AND H₂/SiCl₄ = 1.0 WITH 5% CuCl

FIGURE XV, HYDROCHLORINATION REACTION RATE AT 500 PSIG, 500°C AND H₂/SiCl₄ = 2.8 WITH 5% CuCl

FIGURE XVI, HYDROCHLORINATION REACTION RATE AT 500 PSIG, 450°C AND H₂/SiCl₄ = 2.8 WITH 5% CuCl

FIGURE XVII, HYDROCHLORINATION REACTION RATE AT 500 PSIG, 450°C AND H₂/SiCl₄ = 2.8 WITH 5% CuCl

FIGURE XVIII, HYDROCHLORINATION REACTION RATE AT 300 PSIG, 400°C AND H₂/SiCl₄ = 1.0 WITH 5% CuCl

FIGURE XIX, HYDROCHLORINATION REACTION RATE AT 300 PSIG, 500°C AND H₂/SiCl₄ = 1.0 WITH 2% CuCl

FIGURE XX, EFFECT OF COPPER CATALYST CONCENTRATION ON THE HYDROCHLORINATION REACTION RATE AT 300 PSIG, 500°C AND H₂/SiCl₄ = 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 H₂/SiCl₄ RATIO OF 2.8 AS A FUNCTION OF Si PARTICLE SIZE DISTRIBUTIONS

FIGURE XXIII, HYDROCHLORINATION REACTION RATE AT 300 PSIG, 500°C AND H₂/SiCl₄ 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 H₂/SiCl₄ RATIO OF 2.8

FIGURE XXV, HYDROCHLORINATION REACTION RATE WITH ELECTRONIC GRADE Si AT 500 PSIG, 500°C AND H₂/SiCl₄ 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 H₂/SiCl₄ 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 complementary 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 SiCl₄ and m.g. silicon metal for producing SiHCl₃,

\[3 \text{SiCl}_4 + 2 \text{H}_2 + \text{Si} \rightleftharpoons 4 \text{SiHCl}_3\]  
(1)

One was to collect reaction kinetic data as a function of pressure, temperature and \(\text{H}_2/\text{SiCl}_4\) 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 reaction 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 mg. 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,

$$\text{slow} \hspace{1cm} \text{SiCl}_4 + H_2 \rightarrow \text{SiHCl}_3 + \text{HCl}$$

This is followed by a fast reaction of HCl with silicon on the metal surface to produce more SiHCl$_3$,

$$3 \text{HCl} + \text{Si} \rightarrow \text{SiHCl}_3 + H_2$$

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 occurring 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 lattice.
The effect of a prolonged reaction on the hydrochlorination of SiCl₄ 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 hydrochlorination of SiCl₄ and m.g. silicon metal is an efficient reaction to produce high yield and good conversion of SiHCl₃. 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 SiCl₄ to SiHCl₃. 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 of 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 SiCl₄ and m.g. silicon metal is the front end step in the Union Carbide Silane-to-silicon process represented by the following reaction sequences.

\[
3 \text{SiCl}_4 + 2\text{H}_2 + \text{Si(m.g.)} \rightleftharpoons 4 \text{SiHCl}_3 \quad (1)
\]
\[
2 \text{SiHCl}_3 \rightleftharpoons \text{SiCl}_4 + \text{SiH}_2\text{Cl}_2 \quad (2)
\]
\[
3 \text{SiH}_2\text{Cl}_2 \rightleftharpoons 2 \text{SiHCl}_3 + \text{SiH}_4 \quad (3)
\]
\[
\text{SiH}_4 \xrightarrow{\Delta} 2\text{H}_2 + \text{Si(Solar)} \quad (4)
\]

The hydrochlorination reaction (Equation 1) completes the closed loop process scheme by recycling the by-products, SiCl₄ 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 SiHCl₃ and recycles both the hydrogen and the SiCl₄ generated in the sequent reaction steps. Approximately 60 lb. of SiCl₄ are processed in this step in order to produce one lb. of SiH₄ 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 SiCl₄ and SiHCl₃ 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 SiCl₄ and m.g. silicon metal,

\[ 3 \text{SiCl}_4 + 2\text{H}_2 + \text{Si} \rightleftharpoons 4 \text{SiHCl}_3 \]  

are so chosen as to maximize the formation of trichlorosilane. Interestingly, this reaction was first observed by O. Ruff and K. Albert 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 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 SiHCl₃ is produced. As the law of thermodynamics predicts, higher reactor pressure produces a higher conversion to SiHCl₃. The experimental hydrogenation reactor at MIT is specifically designed to operate at these high pressures in order to optimize the reaction conditions.

A. The Hydrochlorination Apparatus

The apparatus for the hydrochlorination of SiCl₄ and m.g. silicon metal to SiHCl₃ 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 SiCl₄ contained in a stainless steel cylinder. The SiCl₄ 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 H₂/SiCl₄ feed stream can be conveniently selected by adjusting the SiCl₄ liquid temperature and by the applied hydrogen gas pressure. Since the vapor pressure of the SiCl₄ liquid is constant at a given temperature, the H₂/SiCl₄ feed ratio remains constant even though the flowrate of the hydrogen gas varies. The gaseous H₂/SiCl₄ mixture 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 H₂/SiCl₄ 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 H₂/SiCl₄ gaseous mixture. The reactant gas is dispersed into the Si mass bed through a grid 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-point 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 \( \text{H}_2/\text{SiCl}_4 \) 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 \( \text{SiCl}_4 \) and m.g. silicon metal is \( \text{SiHCl}_3 \). The presence of a small amount of \( \text{SiH}_2\text{Cl}_2 \) 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 H₂/ SiCl₄ 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 H₂/ SiCl₄ 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 SiHCl₃ 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 H₂/SiCl₄ 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 % SiHCl₃ conversion versus residence time. The small amount of SiH₂Cl₂ 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 SiHCl₃ increases rapidly with respect to residence times, the curves in Figure III level off at the equilibrium conversion of SiHCl₃. The hydrochlorination reaction rate is defined as the rate at which the conversion of SiHCl₃ 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 H₂/SiCl₄ 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 SiCl₄ and m.g. silicon metal proceeded at a respectable rate to produce 21% conversion of SiHCl₃ 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 SiHCl₃ conversion. The higher equilibrium conversion of SiHCl₃ at higher reaction temperatures is due to a positive free energy of
formation \(\Delta G\) 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 \( \text{H}_2/\text{SiCl}_4 \) ratio obtained under the same reaction conditions at 500°C, 300 psig. The higher conversion of SiHCl$_3$ at a higher \( \text{H}_2/\text{SiCl}_4 \) molar ratio is expected, since the formation of SiHCl$_3$,

\[
3 \text{SiCl}_4 + 2\text{H}_2 + \text{Si} \rightleftharpoons 4 \text{SiHCl}_3
\]

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 \( \text{H}_2/\text{SiCl}_4 \) 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 \( \text{H}_2/\text{SiCl}_4 \) 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 recycled 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 H₂/SiCl₄ 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 SiHCl₃ is somewhat slower at 500 psig than that at 300 psig. For example, at residence time less than 120 seconds, the % SiHCl₃ 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 SiHCl₃ becomes higher at 500 psig than those obtained at 300 psig. This is not unexpected, since the formation of SiHCl₃ results in a net volume contraction as shown in Equation (1). As the reaction approaches equilibrium at long residence times, the formation of product SiHCl₃ 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 H₂/SiCl₄ 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 SiHCl₃ 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% SiHCl₃ while the faster reaction at 300 psig gives 32% SiHCl₃. 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 SiHCl₃ at 300 psig will make about 1,540 lb./hr. of SiHCl₃ 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 SiCl₄ 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, Cu₂O and Cu⁰. A mixture of 160g 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 H₂/SiCl₄ 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 H₂/SiCl₄ 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 H₂/SiCl₄ feed ratio of 2.8. Data in Table XI are presented in Figure X by plotting the % SiHCl₃ conversion and the % SiH₂Cl₂ 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 SiHCl₃ is observed at 30 seconds residence time (solid line). With no copper, the same 23% SiHCl₃ 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 H₂/SiCl₄ 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\textsubscript{4} and m.g. silicon metal to SiHCl\textsubscript{3}. Cuprous chloride, CuCl\textsubscript{1}, is known to react with Si\textsuperscript{(5)} at about 350°C in a displacement reaction,

\[ 4 \text{CuCl} + \text{Si} \xrightarrow{\Delta} \text{SiCl}_4 + 4 \text{Cu} \tag{5} \]

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 lattices 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\textsuperscript{(6)}.

A series of experiments was carried out in the presence of 5 wt\% CuCl\textsubscript{1} 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\textsubscript{1} 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 H₂/SiCl₄ 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 H₂/SiCl₄ feed ratio of 2.8. Data in Table XV are presented in Figure XV by plotting the SiHCl₃ and SiH₂Cl₂ 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 SiH₂Cl₂ 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 H₂/SiCl₄ 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 % SiHCl₃ 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 performs 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 SiCl₄ and m.g. silicon to SiHCl₃ may be postulated as a first slow, rate-determining step on the hydrogen reduction of SiCl₄ to SiHCl₃ 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 SiHCl₃ (Equation 7). The overall reaction, 3 x (6) + (7), gives equation (8) for the hydrochlorination of SiCl₄ and m.g. silicon metal to SiHCl₃.

\[
\text{slow:} \quad \text{SiCl}_4 + H_2 \rightleftharpoons \text{SiHCl}_3 + HCl \quad (6)
\]

\[
\text{fast:} \quad 3\text{HCl} + \text{Si} \rightleftharpoons \text{SiHCl}_3 + H_2 \quad (7)
\]

\[
3 \times (6) + (7) \\
3 \text{SiCl}_4 + 2H_2 + \text{Si} \rightleftharpoons 4 \text{SiHCl}_3 \quad (8)
\]

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 cuprous 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.

\[
4 \text{CuCl + Si}^\circ \xrightarrow{\Delta} \text{SiCl}_4 + 4 \text{Cu}^\circ \quad (9)
\]

\[
\text{Cu}^\circ + \text{Si}^\circ \rightarrow \text{Cu-Si alloy} \quad (10)
\]

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 SiCl₄ may be visualized as a first step chemisorption of SiCl₄ at the Cu-Si sites, viz.,

\[
\begin{array}{c}
\text{Cl} \cdots \text{Si}^3 \\
\vdots \\
\text{Si} - \text{Cu} - \text{Si} - \text{Cu}
\end{array} \quad \text{or} \quad \begin{array}{c}
\text{Cl} \cdots \text{Si}^3 \\
\vdots \\
\text{Cu} - \text{Si} - \text{Cu} - \text{Si}
\end{array}
\]

followed by the reduction of the activated Si--→Cl, Si--→Si and Cu--→Cl linkages by hydrogen to form SiHCl₃ and HCl. This is the slow, rate-determining step occurring 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 SiHCl₃, 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 CH₃Cl + 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 lattices. 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 $H_2/\text{SiCl}_4$ 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 $H_2/\text{SiCl}_4$ feed ratio of 2.8. Reaction kinetic data were collected in the same manner as previous experiments by measuring the rate of $\text{SiHCl}_3$ 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 $\text{SiHCl}_3$ 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 % SiHCl₃ 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 SiCl₄ 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 $\text{SiCl}_4$ 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 $\text{SiHCl}_3$ 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 $\text{H}_2/\text{SiCl}_4$ 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 % $\text{SiHCl}_3$ conversion remains the same.

F. Effect of Impurities in m.g. Silicon Metal

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 viewpoint 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$_2$/SiC$_4$ 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 SiC$_4$ 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 % SiHCl₃ 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 lattices 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 SiCl₄ and m.g. silicon metal to SiHCl₃ were carried out with the object of studying the life of the silicon mass bed. In practice, the hydrochlorination process must be able to substanstain 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. Eventough 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 FeCl₃ (b.p. 315°C) and AlCl₃ (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 SiCl₄ 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 H₂/SiCl₄ 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 SiHCl₃ and SiH₂Cl₂ in the reaction product mixture were measured and recorded. The total amounts of SiH₂Cl₂ and SiHCl₃ 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 % SiHCl₃ 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 % SiHCl₃ 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 H₂/SiCl₄ 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 SiCl₄ and m.g. silicon metal to SiHCl₃,

\[ 3 \text{SiCl}_4 + 2\text{H}_2 + \text{Si} \rightarrow 4 \text{SiHCl}_3 \]  

(9)

A total of 46,659g (103 lb.) of chlorosilane product crude was collected 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 SiH₂Cl₂ and 7,944g (17.5 lb.) of SiHCl₃. The silicon consumption from these two chlorosilane products was calculated according to the above equation (9) for SiHCl₃ and equation (10) below for SiH₂Cl₂,

\[ 2 \text{SiHCl}_3 + 2\text{H}_2 + \text{Si} \rightarrow 3 \text{SiH}_2 \text{Cl}_2 \]  

(10)
The total Si equivalent from 69g of SiH₂Cl₂ and 7,944g of SiHCl₃ 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 SiH₂Cl₂ (b.p. 8°C) and SiHCl₃ (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 hydro-chlorination 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:

<table>
<thead>
<tr>
<th>Element</th>
<th>% in Elutriated Fines</th>
<th>% in M.G. Silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>8.02</td>
<td>0.7</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.82</td>
<td>0.45</td>
</tr>
<tr>
<td>Calcium</td>
<td>1.19</td>
<td>0.05</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.71</td>
<td>0.06</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.15</td>
<td>0.01</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.16</td>
<td>0.01</td>
</tr>
<tr>
<td>Chlorine</td>
<td>7.49</td>
<td></td>
</tr>
<tr>
<td>Silicon (balance)</td>
<td>81.46</td>
<td>98.7</td>
</tr>
</tbody>
</table>

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 AlCl₃ which can be removed along with the liquid chlorosilane crude. Deposition of the white AlCl₃ 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 FeCl₃, 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 resistance 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 epitaxial 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.

<table>
<thead>
<tr>
<th>Element</th>
<th>% in Loose Flakes</th>
<th>% in type 304 Stainless Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>6.61</td>
<td>8 to 11</td>
</tr>
<tr>
<td>Chromium</td>
<td>8.39</td>
<td>18 to 20</td>
</tr>
<tr>
<td>Iron</td>
<td>39.47</td>
<td>72 to 67</td>
</tr>
<tr>
<td>Silicon</td>
<td>17.83</td>
<td>Trace</td>
</tr>
</tbody>
</table>

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 reversible hydrochlorination reaction,

\[
4 \text{SiHCl}_3 \rightleftharpoons 3 \text{SiCl}_4 + 2\text{H}_2 + \text{Si} \tag{10}
\]
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 $\text{H}_2/$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 $\text{H}_2$ 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 11.0 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,

\[ 3 \text{SiCl}_4 + 2 \text{H}_2 + \text{Si} \rightleftharpoons 4 \text{SiHCl}_3 \]  \hspace{1cm} (11)

Equilibrium Constant, \( K = \frac{(\text{SiHCl}_3)^4}{(\text{SiCl}_4)^3(\text{H}_2)^2} \)

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 occurring 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.

\[ \text{Si} + 3 \text{HCl} \leftrightarrow \text{SiHCl}_3 + \text{H}_2 \]  

(12)

\[ 2 \text{Fe} + 6 \text{HCl} \leftrightarrow 2 \text{FeCl}_3 + 3 \text{H}_2 \]  

(13)

\[ \text{Ni} + 2 \text{HCl} \leftrightarrow \text{NiCl}_2 + \text{H}_2 \]  

(14)

\[ 2 \text{Cr} + 6 \text{HCl} \leftrightarrow 2 \text{CrCl}_3 + 3 \text{H}_2 \]  

(15)

Metal chlorides also are known to react with silicon metal\(^9\)

\[ 4 \text{FeCl}_3 + 3 \text{Si} \leftrightarrow 3 \text{SiCl}_4 + 4 \text{Fe} \]  

(16)

\[ 2 \text{NiCl}_2 + \text{Si} \leftrightarrow \text{SiCl}_4 + 2 \text{Ni} \]  

(17)

\[ 4 \text{CrCl}_3 + 3 \text{Si} \leftrightarrow 3 \text{SiCl}_4 + 4 \text{Cr} \]  

(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 FeCl₃, NiCl₂ and CrCl₃ 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 TiCl₄. Thus, titanium metal is not suitable for the material of construction for the hydrochlorination reactor as previously reported by Union Carbide (4). On the other hand, nickel and chromium produce the least volatile NiCl₂ and CrCl₃ 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 proective 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 SiCl₄ and m.g. silicon metal show that the hydrochlorination process is an efficient reaction to give good conversion and high yield of SiHCl₃. The reaction is very clean and highly specific for the production of SiHCl₃. The only significant by-product is a small amount (1-2%) of SiH₂Cl₂ 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 SiCl₄ and m.g. silicon metal to SiHCl₃. The rate-determining step appears to be the adsorption of SiCl₄ 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 SiHCl₃. 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 lattices 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 evidences shows that the hydrochlorination reaction is primarily a gas-solid reaction. A homogeneous gas phase reaction between SiCl₄ and hydrogen is either very slow or unlikely.

Results of the prolonged reaction between SiCl₄ 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 SiCl₄ 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, FeCl₃, AlCl₃, etc.) may be hydrolysed and the HCl generated can be fed into the hydrochlorination reactor to produce more useful SiHCl₃. 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.

\[ \text{SiHCl}_3 + \text{H}_2 \xrightarrow{1,000^\circ \text{C}} \text{Si, SiCl}_4, \text{HCl, lites,} \text{heavies} \]  

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,

\[ 3 \text{SiCl}_4 + 2\text{H}_2 + \text{Si} \leftrightarrow 4\text{SiHCl}_3 \]  

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 (Cl₃SiSiCl₃) and polysilanes. The Si-Cl represents the lites in Equation (19) which consist of mainly lower boiling SiH₂Cl₂ and SiH₃Cl. The hydrochlorination reaction (Equation 20) fits perfectly into the closed-cycle scheme as shown in Figure XXVIII. First of all, it produces the starting SiHCl₃ for the Siemens reactor. Secondly, it consumes the by-product SiCl₄ generated by the Siemens Process. Thirdly, the same hydrochlorination reactor can be used to recycle HCl to produce more SiHCl₃, viz.,

\[ \text{HCl} + \text{Si} \rightarrow \text{H}_2 + \text{SiHCl}_3 + \text{SiCl}_4 \]  

(21)

The well-known HCl + Si reaction (Equation 21) produces SiHCl₃ and H₂ with a minor amount of SiCl₄. The SiCl₄ and H₂ 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.,

\[ \text{Cl}_3\text{SiSiCl}_3 + \text{H}_2 \rightarrow 2 \text{SiHCl}_3 \]  

(22)

At 500°C, the lites (SiH₂Cl₂, SiH₃Cl) are readily redistributed to the more thermally stable SiCl₄ and SiHCl₃. In essence, all the by-products, major and minor, coming out of the Siemens reactor can be, at least in principle, converted back to SiHCl₃ in the same hydrochlorination reactor as shown in Figure XXVIII.
A distillation/separation step separates the chlorosilane components and the hydrogen gas. Unreacted SiCl₄ is recycled back to the hydrochlorination reactor. The SiHCl₃ and a small amount of SiH₂Cl₂ 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.
VI. REFERENCES


(7) C. Combers, Compt. Rend. 122, 531(1896).


VII APPENDICES

Table I through Table XXVII.

Figure I through Figure XXVIII.
TABLE I

HYDROCHLORINATION OF SiCl₄ AND M.G. SILICON
AT 500 PSIG, 500°C AND H₂/SiCl₄ RATIO 2.8

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Hydrogen Feedrate SCCM⁽¹⁾</th>
<th>Residence Time Second</th>
<th>Reaction mole %</th>
<th>Product</th>
<th>Composition⁽²⁾</th>
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<tbody>
<tr>
<td>1A</td>
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<td>22.2</td>
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<td>69.58</td>
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(1) SCCM Standard C.C. per minute
(2) Average of two or three analyses
TABLE II

HYDROCHLORINATION OF SiCl₄ AND M.G. SILICON
AT 500 PSIG, 450°C AND H₂/SiCl₄ RATIO OF 2.8

<table>
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<th>Experiment No.</th>
<th>Hydrogen Feedrate SCCM(1)</th>
<th>Residence Time Second</th>
<th>Reaction SiH₂Cl₂</th>
<th>Product mole% SiHCl₃</th>
<th>Product mole% SiCl₄</th>
<th>Composition(2) SiCl₄</th>
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(1) SCCM, Standard C.C. per minute
(2) Average of two or three analyses
TABLE III

HYDROCHLORINATION OF SiCl₄ AND M.G. SILICON
AT 500 PSIG, 550°C AND H₂/SiCl₄ RATIO OF 2.8

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<th>Hydrogen Feedrate SCCM</th>
<th>Residence Time Second</th>
<th>Reaction Product mole%</th>
<th>Composition SiCl₄</th>
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TABLE IV

HYDROCHLORINATION OF SiCl₄ AND M.G. SILICON
AT 300 PSIG, 550°C AND H₂/SiCl₄ RATIO OF 1.0

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<thead>
<tr>
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<th>Hydrogen Feedrate SCCM</th>
<th>Residence Time Second</th>
<th>Reaction Product mole%</th>
<th>Composition SiCl₄</th>
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### TABLE V

HYDROCHLORINATION OF SiC₄ AND M.G. SILICON AT

300 PSIG, 500°C AND H₂/SiC₄ RATIO OF 1.0

<table>
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<tr>
<th>Experiment No.</th>
<th>Hydrogen Feedrate SCCM</th>
<th>Residence Time Second</th>
<th>Reaction SiH₂Cl₂</th>
<th>Product mole% SiHCl₃</th>
<th>Composition SiC₄</th>
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TABLE VI

HYDROCHLORINATION OF SiCl₄ AND M.G. SILICON
AT 300 PSIG, 450°C AND H₂/SiCl₄ RATIO OF 1.0

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Hydrogen Feedrate SCCM</th>
<th>Residence Time Second</th>
<th>Reaction SiH₂Cl₂</th>
<th>Product mole% SiHCl₃</th>
<th>Composition SiCl₄</th>
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</thead>
<tbody>
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TABLE VII

HYDROCHLORINATION OF SiCl₄ AND M.G. SILICON
AT 300 PSIG 400°C AND H₂/SiCl₄ RATIO OF 1.0

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<th>Reaction SiH₂Cl₂</th>
<th>Product mole% SiHCl₃</th>
<th>Reaction SiCl₄</th>
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### TABLE VIII

**HYDROCHLORINATION OF SiCl₄ AND M.G. SILICON**

**AT 300 PSIG, 500°C AND H₂/SiCl₄ RATIO OF 2.8**

<table>
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<th>Experiment No.</th>
<th>Hydrogen Feedrate SCCM</th>
<th>Residence Time Second</th>
<th>Reaction SiH₂Cl₂</th>
<th>Product mole% SiHCl₃</th>
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TABLE IX

HYDROCHLORINATION OF SiC\textsubscript{4} AND M.G. SILICON
AT 300 PSIG, 450°C AND H\textsubscript{2}/SiC\textsubscript{4} RATIO OF 2.8

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<th>Experiment No.</th>
<th>Hydrogen Feedrate SCCM</th>
<th>Residence Time Second</th>
<th>Reaction SiH\textsubscript{2}Cl\textsubscript{2}</th>
<th>Product mole% SiHCl\textsubscript{3}</th>
<th>Product mole% SiCl\textsubscript{4}</th>
<th>Composition SiCl\textsubscript{4}</th>
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<tr>
<td>4</td>
<td>884</td>
<td>59.5</td>
<td>0.541</td>
<td>24.72</td>
<td>74.75</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>680</td>
<td>77.4</td>
<td>0.650</td>
<td>26.70</td>
<td>72.64</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>455</td>
<td>116</td>
<td>0.860</td>
<td>28.55</td>
<td>70.56</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>263</td>
<td>200</td>
<td>1.070</td>
<td>31.32</td>
<td>67.61</td>
<td></td>
</tr>
</tbody>
</table>
TABLE X

HYDROCHLORINATION OF SiCl₄ AND M.G. SILICON
AT 300 PSIG, 400°C AND H₂/SiCl₄ RATIO OF 2.8

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Hydrogen Feedrate SCCM</th>
<th>Residence Time Second</th>
<th>Reaction SiH₂Cl₂</th>
<th>Product mole% SiHCl₃</th>
<th>Composition SiCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2454</td>
<td>21.7</td>
<td>~0</td>
<td>8.519</td>
<td>91.48</td>
</tr>
<tr>
<td>2</td>
<td>1640</td>
<td>32.4</td>
<td>&lt;0.02</td>
<td>12.52</td>
<td>87.49</td>
</tr>
<tr>
<td>3</td>
<td>838</td>
<td>63.4</td>
<td>0.063</td>
<td>14.96</td>
<td>84.98</td>
</tr>
<tr>
<td>4</td>
<td>485</td>
<td>110</td>
<td>0.324</td>
<td>20.41</td>
<td>79.27</td>
</tr>
<tr>
<td>5</td>
<td>219</td>
<td>243</td>
<td>0.663</td>
<td>25.26</td>
<td>74.08</td>
</tr>
</tbody>
</table>
TABLE XI

HYDROCHLORINATION OF SiCl₄ AND M.G. SILICON
AT 500 PSIG, 500°C AND H₂/SiCl₄ RATIO OF 2.8
WITH 5% CEMENT COPPER

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Hydrogen Feedrate SCCM (1)</th>
<th>Residence Time Second</th>
<th>Reaction SiH₂Cl₂</th>
<th>Product mole% (2) SiHCl₃</th>
<th>Composition SiCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1735</td>
<td>34.9</td>
<td>1.005</td>
<td>30.06</td>
<td>68.91</td>
</tr>
<tr>
<td>2</td>
<td>1195</td>
<td>50.6</td>
<td>1.126</td>
<td>33.56</td>
<td>65.31</td>
</tr>
<tr>
<td>3</td>
<td>790</td>
<td>76.5</td>
<td>1.277</td>
<td>35.50</td>
<td>63.23</td>
</tr>
<tr>
<td>4</td>
<td>395</td>
<td>153</td>
<td>1.305</td>
<td>36.26</td>
<td>62.44</td>
</tr>
<tr>
<td>5</td>
<td>210</td>
<td>288</td>
<td>1.482</td>
<td>38.10</td>
<td>60.42</td>
</tr>
</tbody>
</table>

(1) SCCM, Standard c.c. per minute
(2) Average of two or three analyses
TABLE XII

HYDROCHLORINATION OF SiCl₄ AND M.G. SILICON
AT 500 PSIG, 450°C AND H₂/SiCl₄ RATIO OF 2.8
WITH 5% CEMENT COOPER

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Hydrogen Feedrate SCCM(1)</th>
<th>Residence Time Second</th>
<th>Reaction Product mole% (2) SiH₂Cl₂ SiHCl₃</th>
<th>Composition SiCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1715</td>
<td>34.9</td>
<td>0.711</td>
<td>24.02</td>
</tr>
<tr>
<td>2</td>
<td>1105</td>
<td>54.2</td>
<td>0.856</td>
<td>29.06</td>
</tr>
<tr>
<td>3</td>
<td>657</td>
<td>91.2</td>
<td>0.968</td>
<td>31.88</td>
</tr>
<tr>
<td>4</td>
<td>390</td>
<td>154</td>
<td>1.148</td>
<td>33.86</td>
</tr>
<tr>
<td>5</td>
<td>193</td>
<td>310</td>
<td>1.290</td>
<td>35.79</td>
</tr>
</tbody>
</table>

(1) SCCM, Standard c.c. per minute
(2) Average of two or three analyses
TABLE XIII

HYDROCHLORINATION OF SiCl\textsubscript{4} AND M.G. SILICON AT 300 PSIG, 500°C AND H\textsubscript{2}/SiCl\textsubscript{4} RATIO OF 1.0 WITH 5% CEMENT COPPER

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Hydrogen Feedrate SCCM(^{(1)})</th>
<th>Residence Time Second</th>
<th>Reaction Product mole(^{(2)})</th>
<th>Composition SiCl\textsubscript{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1552</td>
<td>13.7</td>
<td>0.616</td>
<td>78.53</td>
</tr>
<tr>
<td>2</td>
<td>1158</td>
<td>18.3</td>
<td>0.622</td>
<td>77.66</td>
</tr>
<tr>
<td>3</td>
<td>705</td>
<td>30.1</td>
<td>0.719</td>
<td>75.61</td>
</tr>
<tr>
<td>4</td>
<td>382</td>
<td>55.5</td>
<td>0.792</td>
<td>72.19</td>
</tr>
<tr>
<td>5</td>
<td>187</td>
<td>113</td>
<td>1.049</td>
<td>69.77</td>
</tr>
</tbody>
</table>

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

(2) Average of two or three analyses
TABLE XIV

HYDROCHLORINATION OF SiCl₄ AND M.G. SILICON

AT 300 PSIG, 500°C AND H₂/SiCl₄ RATIO OF 2.8

WITH 5% CEMENT COPPER

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Hydrogen Feedrate SCCM (1)</th>
<th>Residence Time Second</th>
<th>Reaction SiH₂Cl₂</th>
<th>Product mole% (2) SiHCl₃</th>
<th>Composition SiCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1750</td>
<td>16.6</td>
<td>0.861</td>
<td>28.19</td>
<td>70.95</td>
</tr>
<tr>
<td>2</td>
<td>1288</td>
<td>22.6</td>
<td>0.969</td>
<td>29.91</td>
<td>69.13</td>
</tr>
<tr>
<td>3</td>
<td>690</td>
<td>42.1</td>
<td>1.125</td>
<td>33.06</td>
<td>65.82</td>
</tr>
<tr>
<td>4</td>
<td>386</td>
<td>75.4</td>
<td>1.416</td>
<td>35.21</td>
<td>63.37</td>
</tr>
<tr>
<td>5</td>
<td>150</td>
<td>194</td>
<td>1.626</td>
<td>38.06</td>
<td>60.31</td>
</tr>
</tbody>
</table>

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

(2) Average of two or three analyses
TABLE XV

HYDROCHLORINATION OF SiCl₄ AND M.G. SILICON
AT 500 PSIG, 500°C AND H₂/SiCl₄ RATIO OF 2.8
WITH 5% CUPROUS CHLORIDE

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Hydrogen Feedrate SCCM (1)</th>
<th>Residence Time Second</th>
<th>Reaction SiH₂Cl₂</th>
<th>Product mole¹(2) SiH₄Cl₃</th>
<th>Composition SiCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1780</td>
<td>44.9</td>
<td>1.404</td>
<td>34.13</td>
<td>64.47</td>
</tr>
<tr>
<td>2</td>
<td>1246</td>
<td>64.2</td>
<td>1.450</td>
<td>37.98</td>
<td>60.57</td>
</tr>
<tr>
<td>3</td>
<td>770</td>
<td>104</td>
<td>1.610</td>
<td>39.23</td>
<td>59.16</td>
</tr>
<tr>
<td>4</td>
<td>370</td>
<td>216</td>
<td>1.977</td>
<td>41.28</td>
<td>56.74</td>
</tr>
<tr>
<td>5</td>
<td>237</td>
<td>338</td>
<td>2.271</td>
<td>41.38</td>
<td>56.35</td>
</tr>
</tbody>
</table>

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

(2) Average of two or three analyses
TABLE XVI

HYDROCHLORINATION OF SiCl₄ AND M.G. SILICON
AT 500 PSIG, 450°C AND H₂/SiCl₄ RATIO OF 2.8
WITH 5% CUPROUS CHLORIDE

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Hydrogen Feedrate (SCCM)</th>
<th>Residence Time (Second)</th>
<th>Reaction Product mole%</th>
<th>Composition SiCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1782</td>
<td>46.4</td>
<td>0.925</td>
<td>29.93</td>
</tr>
<tr>
<td>2</td>
<td>1244</td>
<td>66.5</td>
<td>1.240</td>
<td>32.88</td>
</tr>
<tr>
<td>3</td>
<td>692</td>
<td>120</td>
<td>1.504</td>
<td>35.32</td>
</tr>
<tr>
<td>4</td>
<td>382</td>
<td>216</td>
<td>1.446</td>
<td>38.92</td>
</tr>
<tr>
<td>5</td>
<td>222</td>
<td>373</td>
<td>2.074</td>
<td>39.39</td>
</tr>
</tbody>
</table>

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

(2) Average of two or three analyses
TABLE XVII

HYDROCHLORINATION OF SiCl₄ AND M.G. SILICON
AT 300 PSIG, 500°C AND H₂/SiCl₄ RATIO OF 1.0
WITH 5% CUPROUS CHLORIDE

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Hydrogen Feedrate SCCM (1)</th>
<th>Residence Time Second</th>
<th>Reaction SiH₂Cl₂</th>
<th>Product mole% (2) SiHCl₃</th>
<th>Composition SiCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1550</td>
<td>18.2</td>
<td>0.461</td>
<td>21.86</td>
<td>77.68</td>
</tr>
<tr>
<td>2</td>
<td>1037</td>
<td>27.2</td>
<td>0.574</td>
<td>23.63</td>
<td>75.81</td>
</tr>
<tr>
<td>3</td>
<td>700</td>
<td>40.2</td>
<td>0.923</td>
<td>26.55</td>
<td>72.53</td>
</tr>
<tr>
<td>4</td>
<td>390</td>
<td>72.2</td>
<td>0.944</td>
<td>28.64</td>
<td>70.42</td>
</tr>
<tr>
<td>5</td>
<td>147</td>
<td>192</td>
<td>1.311</td>
<td>31.02</td>
<td>67.68</td>
</tr>
</tbody>
</table>

(1) SCCM, Standard c.c. per minute
(2) Average of two or three analyses
TABLE XVIII

HYDROCHLORINATION OF SiCl₄ AND M.G. SILICON
AT 300 PSIG, 400°C AND H₂/SiCl₄ RATIO OF 1.0
WITH 5% CUPROUS CHLORIDE

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Hydrogen Feedrate SCCM (1)</th>
<th>Residence Time Second</th>
<th>Reaction mole%</th>
<th>Product mole% (2)</th>
<th>Composition SiCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1908</td>
<td>18.3</td>
<td>0.078</td>
<td>9.91</td>
<td>90.02</td>
</tr>
<tr>
<td>2</td>
<td>1406</td>
<td>24.8</td>
<td>0.100</td>
<td>11.42</td>
<td>88.49</td>
</tr>
<tr>
<td>3</td>
<td>789</td>
<td>44.1</td>
<td>0.189</td>
<td>15.94</td>
<td>83.88</td>
</tr>
<tr>
<td>4</td>
<td>458</td>
<td>76.0</td>
<td>0.277</td>
<td>19.09</td>
<td>80.64</td>
</tr>
<tr>
<td>5</td>
<td>254</td>
<td>137</td>
<td>0.435</td>
<td>21.92</td>
<td>77.65</td>
</tr>
<tr>
<td>6</td>
<td>135</td>
<td>258</td>
<td>0.599</td>
<td>25.90</td>
<td>73.50</td>
</tr>
</tbody>
</table>

(1) SCCM, Standard c.c. per minute
(2) Average of two or three analyses
**TABLE XIX**

HYDROCHLORINATION OF SiCl₄ AND M.G. SILICON

AT 300 PSIG, 500°C AND H₂/SiCl₄ = 1.0 WITH 2% CuCl

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Hydrogen Feedrate (SCCM)</th>
<th>Residence Time (Second)</th>
<th>Reaction SiH₂Cl₂ Mole%</th>
<th>Product SiHCl₃ Mole%</th>
<th>Composition SiCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1350</td>
<td>21.5</td>
<td>0.4644</td>
<td>21.98</td>
<td>77.56</td>
</tr>
<tr>
<td>2</td>
<td>940</td>
<td>30.9</td>
<td>0.5206</td>
<td>23.58</td>
<td>75.91</td>
</tr>
<tr>
<td>3</td>
<td>620</td>
<td>46.8</td>
<td>0.7516</td>
<td>27.05</td>
<td>72.21</td>
</tr>
<tr>
<td>4</td>
<td>220</td>
<td>132</td>
<td>1.040</td>
<td>30.25</td>
<td>68.71</td>
</tr>
</tbody>
</table>

(1) SCCM, Standard c.c. per minute
<table>
<thead>
<tr>
<th>Tyler Mesh No.</th>
<th>Particle Size Range (μm)</th>
<th>Mean Particle Size (μm)</th>
<th>Relative Surface Area</th>
<th>Bulk Density Compact</th>
<th>Bulk Density Loose</th>
<th>Average Density Void Space</th>
</tr>
</thead>
<tbody>
<tr>
<td>32 x 65</td>
<td>65 x 150 = 1.0</td>
<td>0.45</td>
<td>355</td>
<td>1.39</td>
<td>1.29</td>
<td>1.14</td>
</tr>
<tr>
<td>65 x 150</td>
<td>500 x 210 = 1.0</td>
<td>1.00</td>
<td>158</td>
<td>1.24</td>
<td>1.19</td>
<td>1.07</td>
</tr>
<tr>
<td>105 x 37</td>
<td>150 x 400 = 1.0</td>
<td>2.23</td>
<td>71</td>
<td>1.24</td>
<td>1.07</td>
<td>1.16</td>
</tr>
</tbody>
</table>

(1) μm, micrometer = microns
TABLE XXI

HYDROCHLORINATION OF SiCl₄ WITH 32 x 65 MESH M.G. Si AT 500 PSIG, 500°C AND H₂/SiCl₄ = 2.8

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Hydrogen Feedrate SCCM (1)</th>
<th>Residence Time Second</th>
<th>Reaction mole%</th>
<th>Product mole%</th>
<th>Composition SiCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1767</td>
<td>28.8</td>
<td>0.615</td>
<td>25.16</td>
<td>74.23</td>
</tr>
<tr>
<td>2</td>
<td>1186</td>
<td>42.9</td>
<td>0.786</td>
<td>27.88</td>
<td>71.34</td>
</tr>
<tr>
<td>3</td>
<td>618</td>
<td>82.3</td>
<td>1.004</td>
<td>31.44</td>
<td>67.56</td>
</tr>
<tr>
<td>4</td>
<td>328</td>
<td>155</td>
<td>1.273</td>
<td>33.30</td>
<td>65.43</td>
</tr>
<tr>
<td>5</td>
<td>175</td>
<td>290</td>
<td>1.162</td>
<td>35.09</td>
<td>63.75</td>
</tr>
</tbody>
</table>

(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

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Hydrogen Feedrate SCCM$^{(1)}$</th>
<th>Residence Time Second</th>
<th>Reaction SiH$_2$Cl$_2$</th>
<th>Product mole% SiHCl$_3$</th>
<th>Composition SiCl$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1489</td>
<td>50.9</td>
<td>1.086</td>
<td>31.18</td>
<td>67.74</td>
</tr>
<tr>
<td>2</td>
<td>1015</td>
<td>75.2</td>
<td>1.190</td>
<td>33.52</td>
<td>65.29</td>
</tr>
<tr>
<td>3</td>
<td>649</td>
<td>118</td>
<td>1.218</td>
<td>34.20</td>
<td>64.59</td>
</tr>
<tr>
<td>4</td>
<td>347</td>
<td>220</td>
<td>1.564</td>
<td>36.20</td>
<td>62.24</td>
</tr>
<tr>
<td>5</td>
<td>191</td>
<td>400</td>
<td>1.723</td>
<td>37.84</td>
<td>60.44</td>
</tr>
</tbody>
</table>

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

HYDROCHLORINATION OF SiCl₄ AND 150 x 400 MESH M.G.
Si AT 300 PSIG, 500°C AND H₂/SiCl₄ = 1.0

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Hydrogen Feedrate SCCM⁽¹⁾</th>
<th>Residence Time Second</th>
<th>Reaction mole%</th>
<th>Product mole%</th>
<th>Composition SiCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1058</td>
<td>32.7</td>
<td>0.3501</td>
<td>20.52</td>
<td>79.13</td>
</tr>
<tr>
<td>2</td>
<td>716</td>
<td>48.3</td>
<td>0.4318</td>
<td>21.79</td>
<td>77.79</td>
</tr>
<tr>
<td>3</td>
<td>425</td>
<td>81.3</td>
<td>0.5152</td>
<td>24.62</td>
<td>74.86</td>
</tr>
<tr>
<td>4</td>
<td>168</td>
<td>206</td>
<td>0.6550</td>
<td>25.76</td>
<td>73.59</td>
</tr>
</tbody>
</table>

⁽¹⁾ SCCM, Standard c.c. per minute
**TABLE XXIV**

HYDROCHLORINATION OF $\text{SiCl}_4$ AND 32 x 65 MESH

M.G. Si AT 300 PSIG, 500°C AND $\text{H}_2/\text{SiCl}_4 = 1.0$

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Hydrogen Feedrate SCCM (1)</th>
<th>Residence Time Second</th>
<th>Reaction SiH$_2$Cl$_2$</th>
<th>Product mole% SiHC$_3$</th>
<th>Composition SiCl$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1760</td>
<td>12.9</td>
<td>0.1527</td>
<td>14.55</td>
<td>85.30</td>
</tr>
<tr>
<td>2</td>
<td>1230</td>
<td>18.5</td>
<td>0.2137</td>
<td>17.00</td>
<td>82.78</td>
</tr>
<tr>
<td>3</td>
<td>626</td>
<td>36.4</td>
<td>0.2784</td>
<td>20.50</td>
<td>79.23</td>
</tr>
<tr>
<td>4</td>
<td>315</td>
<td>72.3</td>
<td>0.4356</td>
<td>23.19</td>
<td>76.38</td>
</tr>
<tr>
<td>5</td>
<td>158</td>
<td>144</td>
<td>0.5277</td>
<td>24.63</td>
<td>74.84</td>
</tr>
</tbody>
</table>

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

HYDROCHLORINATION OF SiCl₄ AND ELECTRONIC GRADE
Si TO SiHCl₃ AT 500 PSIG, 500°C AND
H₂/SiCl₄ Ratio of 2.8

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Hydrogen Feedrate SCCM⁽¹⁾</th>
<th>Residence Time Second</th>
<th>Reaction SiH₂Cl₂</th>
<th>Product mole% SiHCl₃</th>
<th>Product mole% SiCl₄</th>
<th>Composition SiCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1200</td>
<td>71.3</td>
<td>0.2982</td>
<td>10.19</td>
<td>89.51</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>800</td>
<td>107</td>
<td>0.3507</td>
<td>12.71</td>
<td>86.94</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>415</td>
<td>207</td>
<td>0.2990</td>
<td>16.86</td>
<td>82.84</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>205</td>
<td>419</td>
<td>0.6389</td>
<td>25.70</td>
<td>73.66</td>
<td></td>
</tr>
</tbody>
</table>

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

HYDROCHLORINATION OF SiCl₄ AND ELECTRONIC GRADE Si METAL WITH 5% CuCl ADDED AT 500 PSIG, 500°C AND H₂/SiCl₄ = 2.8

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Hydrogen Feedrate SCCM(1)</th>
<th>Residence Time Second</th>
<th>Reaction SiH₂Cl₂</th>
<th>Product mole% SiHCl₃</th>
<th>Composition SiCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1417</td>
<td>50.1</td>
<td>1.756</td>
<td>34.58</td>
<td>63.67</td>
</tr>
<tr>
<td>2</td>
<td>1009</td>
<td>70.4</td>
<td>1.652</td>
<td>36.32</td>
<td>62.03</td>
</tr>
<tr>
<td>3</td>
<td>542</td>
<td>131</td>
<td>1.817</td>
<td>38.40</td>
<td>59.78</td>
</tr>
<tr>
<td>4</td>
<td>309</td>
<td>231</td>
<td>1.704</td>
<td>40.08</td>
<td>58.21</td>
</tr>
</tbody>
</table>

(1) SCCM, Standard c.c. per minute
### TABLE XXVII

HYDROCHLORINATION OF SiCl₄ AND M.G. Si AT 500°C,
300 PSIG AND H₂/SiCl₄ = 2.0

<table>
<thead>
<tr>
<th>Experiment Date</th>
<th>Cumulative Reaction Time Hour</th>
<th>Silicon Mass Bed g.</th>
<th>Hydrogen Feedrate SCCM</th>
<th>Residence Time Second</th>
<th>SiH₂Cl₂ mole%</th>
<th>SiHCl₃ mole%</th>
</tr>
</thead>
<tbody>
<tr>
<td>8/28/80</td>
<td>25</td>
<td>151.7</td>
<td>1340</td>
<td>31.2</td>
<td>0.4084</td>
<td>22.30</td>
</tr>
<tr>
<td>9/10/80</td>
<td>65</td>
<td>136.4</td>
<td>1146</td>
<td>32.8</td>
<td>0.3641</td>
<td>22.53</td>
</tr>
<tr>
<td>10/20/80</td>
<td>155</td>
<td>126.3</td>
<td>1070</td>
<td>32.5</td>
<td>0.4809</td>
<td>22.10</td>
</tr>
<tr>
<td>10/28/80</td>
<td>183</td>
<td>129.8</td>
<td>1080</td>
<td>33.1</td>
<td>0.4049</td>
<td>21.87</td>
</tr>
<tr>
<td>11/07/80</td>
<td>229</td>
<td>129.5</td>
<td>1090</td>
<td>32.7</td>
<td>0.4357</td>
<td>22.35</td>
</tr>
</tbody>
</table>
FIGURE 1  Apparatus For The Hydrogenation Of SiCl₄ To SiHCl₃
FIGURE II  \( H_2/\text{SiCl}_4 \) Gaseous Inlet to Reactor and Grid Design

- Reactor Tube 1-1/4" O.D. x 1/8" Wall
- Reactor Grid Welded to S.St. Block
- Stainless Steel Block 15/16" Dia. x 5" Long
  Machine To Shape As Shown
- 3/8" S.St. Tubing For \( H_2/\text{SiCl}_4 \)
  Inlet, Flared At Top To Hold S.St. Block
- 1-1/4" Stainless Steel Swagelok Cap
- 3/8" Swagelok Male Connector

5-Orifice Grid Design
Orifice = 0.05"
x = 1/5"
3 SiCl₄ + 2H₂ + Si ⇌ 4 SiHCl₃

FIGURE III HYDROCHLORINATION OF SiCl₄ AT 500 PSIG, H₂/SiCl₄ RATIO OF 2.8
FIGURE IV HYDROCHLORINATION OF SiCl$_4$ AT 300 PSIG, H$_2$/SiCl$_4$ RATIO OF 1.0

$3\text{SiCl}_4 + 2\text{H}_2 \rightarrow 4\text{SiHCl}_3$
**Figure V** Hydrogenation of SiCl₄ at 300 psig and H₂/SiCl₄ ratio of 2.8

The graph shows the conversion of SiCl₄ as a function of residence time for temperatures of 500°C, 450°C, and 400°C. The reaction studied is:

\[3 \text{SiCl}_4 + 2\text{H}_2 + \text{Si} \rightarrow 4\text{SiHCl}_3\]
FIGURE VI  EFFECT OF $\text{H}_2 : \text{SiCl}_4$ RATIO AT 500°C, 300 PSIG
**Figure VII**

Effect of pressure on the reaction rate at 450°C, 
$H_2/\text{SiCl}_4$ ratio of 2.8
FIGURE VIII  EFFECT OF PRESSURE ON THE REACTION RATE AT 500°C, 
H₂/SiCl₄ RATIO OF 2.8
With cement type copper an induction period of 15-20 hours was observed.

- Si mass bed @ ~ 38% conversion
- Si mass bed @ ~ 18% conversion
- Fresh Si mass bed @ 0% conversion
- No copper bed @ ~ 20% conversion

**Figure IX** Hydrochlorination of SiCl₄ at 300 psig, 500°C and H₂/SiCl₄ = 1.0 with 5% cement copper catalyst.
FIGURE 1 HYDROCHLORINATION OF SiCl₄ AND M.G. SILICON AT 500 PSIG, 500°C AND H₂/SiCl₄ 2.8 WITH 5% CEMENT COPPER
FIGURE XI  HYDROCHLORINATION OF SiCl\textsubscript{4} AT 500 PSIG, 450\textdegree C AND H\textsubscript{2}/SiCl\textsubscript{4}=2.8 WITH AND WITHOUT COPPER CATALYST
FIGURE XII  HYDROCHLORINATION OF SiCl$_4$ AT 300PSIG, 500°C AND H$_2$/SiCl$_4$=1.0 WITH AND WITHOUT COPPER CATALYST
FIGURE XIII  HYDROCHLORINATION OF SiCl₄ AT 300 PSIG, 500°C AND H₂/SiCl₄=2.8 WITH AND WITHOUT COPPER CATALYST
"REACTIVE" CuC\textsubscript{2} CATALYST SHOWED ESSENTIALLY NO INDUCTION PERIOD

**FIGURE XIV** HYDROCHLORINATION OF SiCl\textsubscript{4} AT 300 PSIG, 500°C AND H\textsubscript{2}/SiCl\textsubscript{4} = 1.0 WITH 5% CuC\textsubscript{2} CATALYST
FIGURE XIV HYDROCHLORINATION OF SiC\textsubscript{4} AT 500 PSIG, 500°C AND H\textsubscript{2}/SiC\textsubscript{4}=2.8 WITH AND WITHOUT COPPER CATALYST
FIGURE XVI  HYDROCHLORINATION OF SiCl₄ AT 500 PSIG, 450°C AND H₂/SiCl₄=2.8 WITH AND WITHOUT COPPER CATALYST
Figure XVII  Hydrochlorination of SiC₄ at 300 psig, 500°C and H₂/SiC₄ = 1.0 with and without copper catalyst.
FIGURE XVIII HYDROCHLORINATION OF SiCl₄ AT 300 PSIG, 400°C AND H₂/SiCl₄=1.0 WITH AND WITHOUT COPPER CATALYST
FIGURE XIX HYDROCHLORINATION OF SiCl₄ AT 300 PSIG, 500°C AND H₂/SiCl₄ = 1.0 WITH 2% CuCl₂ INITIALLY ADDED
FIGURE XX HYDROCHLORINATION OF SiCl₄ AT 300 PSIG, 500°C AND H₂/SiCl₄ = 1.0 WITH 2% AND 5% CuCl₂ 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 SiCl₄ AND M. G. Si AT 500°C AND H₂/SiCl₄ RATIO OF 2.8
FIGURE XXIII PARTICLE SIZE DISTRIBUTION STUDIES: THE HYDROCHLORINATION OF SiCl₄ AND M.G. Si AT 300 PSIG, 500°C AND H₂/SiCl₄ RATIO OF 1.0
FIGURE XXXIV HYDROCHLORINATION OF SiCl₄ TO SiHCl₃ AND Si AT 500 PSIG, 500°C AND H₂/SiCl₄ = 2.8
Figure XXX: Hydrochlorination of SiCl₄ to SiHCl₃ and Si at 500 psig, 500°C and H₂/SiCl₄ = 2.8 with 5% cuprous chloride catalyst.
FIGURE XXVI  PROLONGED REACTION OF SiC$_4$ AND M.G.
SILICON AT 500°C, 300PSIG, H$_2$/SiC$_4$=2.0
WITH AND WITHOUT COPPER ADDED
INCOLOY 800 TEST SAMPLE

HYDROCHLORINATION REACTION

BEFORE = 53.195 g.
AFTER = 53.520 g.
GAIN 0.325 g.

ATMOSPHERIC CORROSION

BEFORE = 12.4026 g.
AFTER = 12.1445 g.
LOSS 0.2581 g.
FIGURE XXVIII  CLOSED-LOOP SIEMENS PROCESS

SIEMENS REACTOR

H₂  98% SiHCL₃, 2% SiH₂Cl₂

POLY Si

HCL

SiCl₄, Si-Si, Si-Cl

H₂

INPUT

M. G. Si

HYDROCHLORINATION REACTOR

SiHCl₃, SiCl₄, H₂

SiH₂Cl₂ SiHCl₃, SiCl₄, H₂

WASTE

DISTILLATION

SiCl₄

SEPARATION

SiHCl₃, SiH₂Cl₂

H₂