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INVESTIGATION OF THE HYDROCHLORINATION OF $SiCl_4$

MASTER

Flat-Plate Solar Array Project. Task 1 Silicon Materials

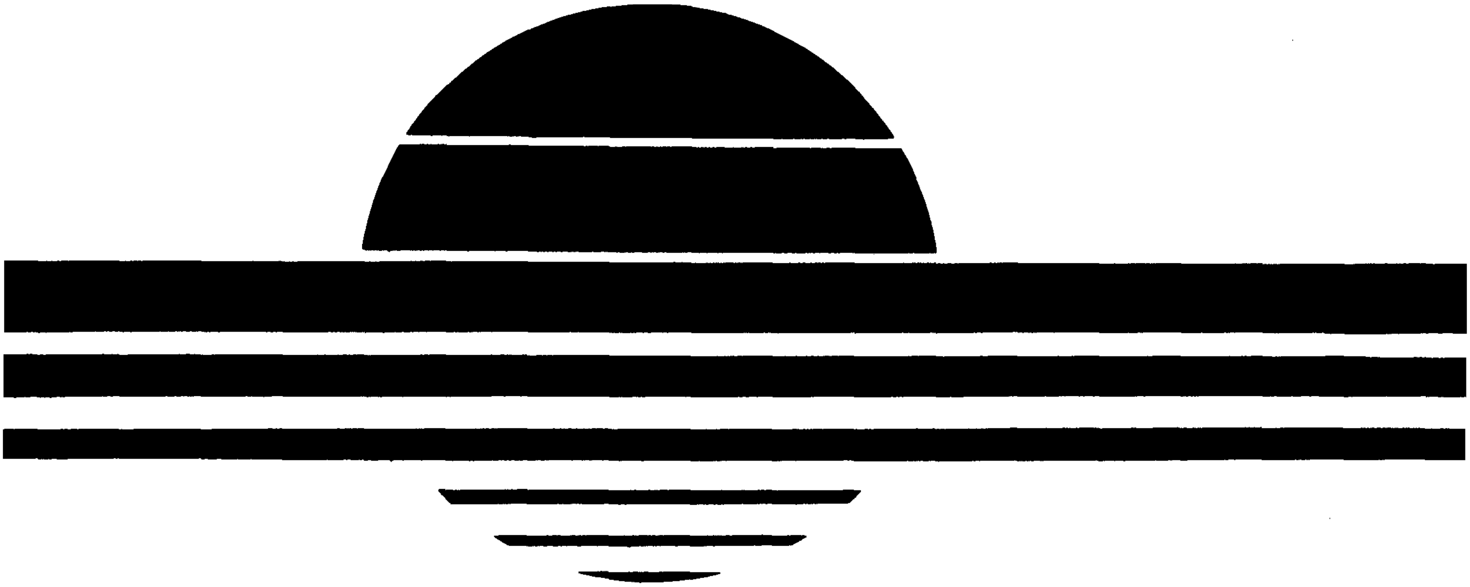
Quarterly Report for the Period July 9—September 30, 1981

By
Jeffrey Y. P. Mui

October 1, 1981

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

Solarelectronics, Inc.
Bellingham, Massachusetts



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FLAT-PLATE SOLAR ARRAY PROJECT

TASK I SILICON MATERIAL

QUARTERLY REPORT

INVESTIGATION OF THE HYDROCHLORINATION OF $SiCl_4$

(Covering the Period July 9, 1981 to September 30, 1981.)

JPL CONTRACT NO. 956061

TO

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

BY

JEFFREY Y. P. MUI

October 1, 1981.

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

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FLAT-PLATE SOLAR ARRAY PROJECT

TASK I SILICON MATERIAL

"Investigation of the Hydrochlorination of $SiCl_4$"

SOLARELECTRONICS, INC.
Bellingham, Mass.
by
Jeffrey Y. P. Mui
October 1, 1981.

ABSTRACT

A program was initiated in July of this year to study the hydrochlorination of silicon tetrachloride and metallurgical grade (m. g.) silicon metal to trichlorosilane,

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

The JPL/Solarelectronics Contract No. 956061 is conducted as a complementary research and development program to supplement the engineering process development activities under the JPL/Union Carbide Contract No. 954334 and the JPL/Hemlock Semiconductor Contract No. 955533. Both the Union Carbide silane-to-silicon process and the Hemlock polysilicon process based on chemical vapor deposition utilize the hydrochlorination reaction as the first step to produce the starting material, trichlorosilane.

A two inch-diameter stainless steel reactor is designed to operate at pressure up to 500 psig and at temperature up to 600°C for the hydrochlorination studies. Experiments are planned to collect reaction kinetic data and to conduct corrosion tests for the material of construction for the hydrochlorination reactor. A concept of recycling HCl gas obtained from the hydrolysis of chloride wastes back to the hydrochlorination reactor will be tested. A four inch-diameter hydrochlorination reactor is planned to conduct experiments for the fluidization study. The merits of a fluidized-bed reactor design and a fixed-bed reactor design will be evaluated.

The design of the hydrochlorination reactor system has been completed. Construction and installation of the hydrochlorination apparatus are in progress.

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I. INTRODUCTION

Work on the JPL/Solarelectronics Contract No. 956061 began in July of this year to study the hydrochlorination of $SiCl_4$ and m.g. Si metal to $SiHCl_3$,

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

This complementary research and development effort is conducted to supplement the engineering process development activities for the Union Carbide silane-to-silicon process and for the Hemlock polysilicon process based on chemical vapor deposition. Both the Union Carbide and the Hemlock process utilize the hydrochlorination reaction (1) as the first step to produce the starting material, $SiHCl_3$, and to recycle the by-product, $SiCl_4$. Currently, the Siemens process practised by the electronics industry for the production of polycrystalline silicon metal also utilizes the same starting material, $SiHCl_3$. The Siemens process also produces $SiCl_4$ as a by-product. Thus, the hydrochlorination reaction (1) is potentially useful to complete a recycle loop for the Siemens polysilicon manufacturing process with substantial savings on raw material cost.(1)

While experimental studies on the hydrochlorination of $SiCl_4$ have been carried out at Union Carbide Corporation (2) and, subsequently, at the Massachusetts Institute of Technology,(1) the JPL Research and Development Contract to Solarelectronics is primarily designed to refine specific engineering design criteria and to evaluate new concepts with the ultimate goal of improving efficiency and to reduce cost. This may include a comprehensive corrosion study to select the most suitable material of construction for the hydrochlorination reactor, a fluidization mechanism study to evaluate the merits of a fluidized-bed and a fixed-bed reactor design and a new concept to recycle waste chloride by-products.

II. DISCUSSION

A. Program Plan

The attached Program Plan summarizes the one-year experimental program on the hydrochlorination of $SiCl_4$ and m.g. silicon to $SiHCl_3$. A two inch-diamater stainless steel reactor system will be constructed within the first four months of the contract. Reaction kinetic measurements and a mass balance on the hydrochlorination reaction will be made to co-relate the experimental results to previously obtained reaction rate data. At the same time, impurities in the chlorosilane products are identified and measured. Then, a comprehensive corrosion study will be conducted to test a variety of conventional metal alloys as the material of construction for the hydrochlorination reactor. Based on the corrosion test results, attempts will be made to select the most suitable material of construction for the hydrochlorination reactor on a cost-effectiveness basis.

A four inch-diameter hydrochlorination reactor will be designed and installed by the 9th month of the contract work. The 4 inch reactor replaces the 2 inch reactor in the same hydrochlorination apparatus. The 4 inch reactor is designed to operate at a reduced pressure of about 60 psig. At 60 psig, the four inch reactor has approximately the same throughput as the two inch reactor operating at 500 psig under similar reaction conditions. The larger 4 inch reactor will provide a much better quality of fluidization than the smaller one inch-diameter and the two inch-diameter reactor used in the previous experimental studies. Reaction rate measurements will be made with the 4 inch reactor operating at both the fluidized-bed mode and the fixed-bed mode. Based on the reaction kinetic measurements, a evaluation will be made on the merits of a fluidized-bed reactor design versus a fixed-bed reactor design.

Finally, recommendations will be made to JPL on the optimization of the hydrochlorination process and on areas for additional development work.

B. The Hydrochlorination Apparatus

Design of the two inch-diameter hydrochlorination reactor has been completed. The hydrochlorination apparatus is schematically shown in Figure I. A continuous flow of hydrogen gas is fed from a hydrogen gas cylinder. The pressure regulator reduces the cylinder pressure to approximately 50 psig above the selected pressure for the hydrochlorination reaction. The ΔP provides the driving force for the mass flow through the reactor system. A fine metering valve controls the flowrate of the hydrogen gas. The gaseous flowrate is measured by a Mass Flowmeter/Controller (Matheson, Model No. 8240-0450). An automatic feed mechanism may be used in place of the fine metering valve so that the hydrogen feedrate is maintained at a constant value by the Mass Flowmeter/Controller. The hydrogen gas is mixed with the $SiCl_4$ vapor to give the desired $H_2/SiCl_4$ molar ratio for the hydrochlorination reaction. The gaseous $H_2/SiCl_4$ mixture is fed into the bottom of the hydrochlorination reactor.

(1) The $H_2/SiCl_4$ Feed

Two methods are used to obtain the desired feed ratio of hydrogen gas and $SiCl_4$. One method involves the passage of the hydrogen gas stream into a hot liquid column of $SiCl_4$ contained in a stainless steel cylinder as shown in Figure I. The $SiCl_4$ liquid column is heated by circulation a heat transfer fluid from a constant temperature bath through the jacket on the stainless steel cylinder. The hydrogen gas bubbling through the hot $SiCl_4$ liquid is saturated with $SiCl_4$ vapor. Since the vapor pressure of $SiCl_4$ is constant at a given temperature, a constant ratio of $H_2/SiCl_4$ can be conveniently obtained by controlling the inlet hydrogen gas pressure and by adjusting the temperature of the $SiCl_4$ liquid. The $SiCl_4$ liquid inside the stainless steel cylinder is maintained at a constant level by the automatic $SiCl_4$ feed mechanism. A liquid level indicator/controller (Princo Instruments, Model S900 Indicating Controller) with a capacitance probe is used to measure and to add fresh $SiCl_4$ into the $SiCl_4$ Re-fill Unit as shown in Figure I. As long as sufficient residence time in the feed tank is allowed for the hydrogen gas, the $H_2/SiCl_4$ ratio does not change with the hydrogen gas flowrate. In this case, a state of dynamic equilibrium is reached between the H_2 gas and the hot $SiCl_4$ liquid. Thus, one only needs to control the H_2 gas flowrate in order to obtain the desired total gaseous $H_2/SiCl_4$ feed to the hydrochlorination reactor and the desired $H_2/SiCl_4$ molar ratio.

However, at high $H_2/SiCl_4$ feedrates, a state of equilibrium may not be achievable. Rapid evaporation of the $SiCl_4$ liquid can cause a significant lowering of the $SiCl_4$ liquid temperature to give a higher $H_2/SiCl_4$ molar ratio than expected. This may be the case with the proposed four inch-diameter hydrochlorination reactor for the fluidization mechanism studies. Consequently, a second method of feeding the $H_2/SiCl_4$ mixture into the hydrochlorination reactor is designed. In this method, the $SiCl_4$ liquid from a storage tank is pumped into a vaporizer. The vaporized $SiCl_4$ is mixed with the incoming hydrogen gas injected at the bottom of the vaporizer as shown in Figure I. This method of feeding involves two separated streams, H_2 and $SiCl_4$, Each of these two streams must be maintained constant at the same time in order to obtain the desired $H_2/SiCl_4$ molar ratio. The $H_2/SiCl_4$ vapor mixture is fed into the bottom of the hydrochlorination reactor through heat-traced, connecting tubes.

(2) The Hydrochlorination Reactor

The hydrochlorination reactor is made of Type 304 stainless steel tubing, 2 inches O.D. x 0,188 inch wall. The reactor tube is about 42 inches long. The hydrochlorination reactor design is schematically shown in Figure II. The reactor is electrically heated by four variable auxiliary heaters and by one control heater. The four equally-spaced auxiliary heaters are powered by variable transformers. The power output of these heaters can in individually adjusted so as to compensate for the different degree of heat loss along the reactor tube. Thermocouples are placed at the outside wall of the reactor tube to monitor the temperature at the zones covered by these auxiliary heaters. Uniform temperature along the reactor tube can be achieved by fine adjustments on the power input to these four auxiliary heaters. The auxiliary heaters raise the temperature of the hydrochlorination reactor to several tens of degrees below the desired reaction temperature. The control heater will bring the reactor to the desired reaction temperature. Power input to the control heater is controlled by the Thermo Electric Model Selectrol 700 Process Controller with a thermocouple extending from the top of the reactor to the mid-point of the Si metal mass bed. The Process Controller maintains the reactor at the desired temperature for the hydrochlorination reaction. A ball valve is fitted at the top of the reactor. Fresh silicon metal can be intermittently charged into the reactor through this ball valve. The incoming $H_2/SiCl_4$ vapor mixture is distributed into the Si metal mass bed through a grid plate. The grid plate is a five-orifice design as shown in Figure II.

(3) The In-Line Gas Chromatograph

The reaction product mixture coming out of the hydrochlorination reactor is analyzed by the in-line gas chromatograph which is schematically shown in Figure I. Gaseous sample of the reaction mixture is drawn into the sample loop of the G.C. sampling valve. The sample is injected into the G.C. column by turning the sampling valve to the injection position. The chlorosilane components in the reaction mixture are separated by the G.C. column. The individual components are detected by a standard hot wire detector. The G.C. spectrum is recorded and analyzed by the Hewlett Packard Model 3380s Recorder/Integrator. The hydrochlorination reaction rate is measured as a function of product $SiHCl_3$ conversion versus residence time. A sample line to the in-line gas chromatograph is also provided for the $H_2/SiCl_4$ feed stream before it enters the hydrochlorination reactor. This arrangement allows a direct measurement of the $H_2/SiCl_4$ molar ratio by the in-line gas chromatograph.

(4) The Condenser/Receiver Assembly

The hot reaction mixture coming out of the hydrochlorination reactor is air-cooled through a section of the reactor arm as schematically shown in Figure I. The chlorosilane vapor is condensed by the low temperature condenser. The low temperature condenser is cooled by a refrigeration unit with coolant circulating through its jacket. The liquid chlorosilane products are collected in a 2½ gallon stainless steel cylinder equipped with a liquid level indicator. The liquid level indicator consists a capacitance probe with a signal transmitter and a read-out unit made by Princo Instruments, Inc. Two ball valves are provided to isolate the receiver from the reactor assembly so that the liquid products can be withdrawn from the hydrochlorination apparatus during an experiment. A hydrogen gas inlet and a pressure gauge are provided at the receiver assembly. The receiver can be pressurized with hydrogen gas to the same as the hydrochlorination reactor. The receiver is re-connected to the reactor system by openning the two ball valves.

(5) Hydrogen Gas and Silicon Tetrachloride Recycle

The new hydrochlorination reactor system design provides an option to recycle the unreacted hydrogen gas back to the reactor. This arrangement is useful in studying the effect of organic impurities on the hydrochlorination reaction. In this case, the back pressure regulator is by-passed and the hydrogen gas is recycled back to the reactor by a mechanical pump. The unreacted $SiCl_4$ in the reaction product mixture is also recycled. A distillation unit will be built to recover the unreacted $SiCl_4$

in the reaction product mixture. The recovered $SiCl_4$ is used again in the same hydrochlorination reaction. In this way, the amount of chlorosilane waste is kept at a minimum. With both hydrogen gas and $SiCl_4$ recycled, the accumulation and the distribution of impurities in the overall hydrochlorination process can be studied.

C. Operation Safety

The hydrochlorination apparatus is fitted into a large walk-in hood. This facility much reduces the fire and explosion hazard of the flammable hydrogen gas. It also contains and safely exhausts the corrosive chlorosilane vapor in the case of an accidental spill. The unreacted hydrogen gas coming out of the hydrochlorination reactor is safely disposed of by burning.

(i) The Nature of the Hydrochlorination Reaction

The hydrochlorination of $SiCl_4$ with hydrogen in a mass bed of silicon metal has been shown to be an equilibrium reaction. The reaction is only slightly exothermic to the extent of a few Kcal/mole of Si. The low heat of reaction plus the nature of an equilibrium reaction virtually eliminate the possibility of a violent, run-away reaction. This is an advantage from a safety point of view.

(ii) Pressure Safety Factor

The hydrochlorination apparatus is constructed of stainless steel. To make meaningful reaction rate measurements, the reactor system must be totally leakage-free. High quality Swagelok fittings are used for the construction of the hydrochlorination apparatus. Swagelok fittings require a minimum wall thickness of the stainless steel tubings for a helium leakage-free service. By virtue of this requirement, fairly heavy walled tubings are used to construct the hydrochlorination apparatus. Consequently, the entire reactor system has a safe, nominal operating pressure in excess of 2,000 psig eventhough the experiments on the hydrochlorination reaction is designed to carry out up to 500 psig. Naturally, the hydrochlorination apparatus will be leak-tested and pressure-tested before starting up the hydrochlorination experiments.

(iii) Automatic Alarm System

The hydrochlorination apparatus is semi-automated so that the experiment can be carried out without the need of constant attention. An automatic alarm system is incorporated into the reactor design. A pressure switch (Mercoid Control) with dual set points is connected to the reactor assembly at the low temperature condenser. When an over-pressure (plugging) or an under-pressure (leakage) condition develops, the circuit in the pressure switch is closed to sound of an alarm. The same circuit can also be used to energize a solenoid valve to shut off the hydrogen gas flow. The liquid level indicator/controller provides four liquid level set points. The middle two set points are used to control the $SiCl_4$ liquid level inside the $H_2/SiCl_4$ feed tank as shown in Figure I. The upper and the lower set points are used to set off an alarm when the $SiCl_4$ liquid level is in danger of being over-filled or depleted. The same liquid level indicator/controller for the chlorosilane products receiver is used to sound an alarm when the liquid level in the receiver is in danger of being over-filled. A thermo switch is incorporated into the low temperature condenser assembly. Failure of the cooling system to maintain a low temperature at the condenser sets off an alarm as the rising coolant temperature closes the circuit in the thermo switch.

D. Pollution Control

The unreacted hydrogen gas coming out of the hydrochlorination reactor is safely disposed off by burning in a small combustion chamber. Small amounts of chlorosilane vapor may be present in the unreacted hydrogen gas. An exhaust fan forces the flue gas into a scrubber as shown in Figure I. The silica fume and the acid chloride are removed from the exhaust gas by the scrubber. The scrubber is basically a column with an acid neutralizing solution (aqueous NaOH) circulating through its packing. The small amount of silicate and chloride wastes are collected in the reservoir. The scrubber system removes essentially all the pollutants in the exhaust gas before it is discharged into the atmosphere.

A distillation unit will be built to recover the unreacted $SiCl_4$ in the reaction product mixture obtained from the hydrochlorination experiments. The recovered $SiCl_4$ is used again in the same hydrochlorination reactions. In this way, the amount of chlorosilane wastes are kept at a minimum. The small amounts of metal chloride wastes are collected and stored. With these steps taken, the hydrochlorination experiments can be conducted in an essentially pollution-free enviroment.

E. Summary of Progress

Design of the hydrochlorination apparatus has been completed. The one inch-diameter hydrogenation reactor (under the JPL/MIT Contract No. 955382) was transferred from the Massachusetts Institute of Technology to Solarelectronics, Inc. The reactor assembly will be completely re-built to accommodate the larger two inch-diameter and the four inch-diameter hydrochlorination reactors. Most of the instruments will be re-conditioned for the new hydrochlorination apparatus. Purchase orders for equipment and instrument were sent to selected vendors. Panels for instruments and a metal support structure for the hydrochlorination apparatus were built. Construction and installation of the hydrochlorination apparatus are in progress.

III. PROJECTED SECOND QUARTER ACTIVITIES

Planned activities for the second quarter (October - December) include,

- complete the construction and installation of the hydrochlorination apparatus,
- safety review and start-up reactor,
- carry out experiments on the hydrochlorination of $SiCl_4$,
- collect reaction kinetic data as a function of T, P and $H_2/SiCl_4$ ratio,
- corrosion studies.

IV. REFERENCES

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

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

V. APPENDIX

Program Plan
Figure I - II

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

	Year	1981						1982					
	Month of Year	7	8	9	10	11	12	1	2	3	4	5	6
	Month of Contract	1	2	3	4	5	6	7	8	9	10	11	12
I	Program Plan, Baseline Cost Est.	~~1~~											
II	Transfer Reactor form M.I.T.	~~1~~	~~2~~										
III	Reactor Design, Order Equipment Construction of Apparatus	~~1~~	~~2~~	~~3~~	4								
IV	Safety Review, Start-up Reactor				4								
V	Reaction Kinetics Measurement							▲					
	(1) Function of T, P, C				4	5	6	7					
	(2) Impurities Measurement					5	6	7					
	(3) Mass Balance						6	7					
VI	Corrosion Study									▲			
	(1) Type 304,316 S.St., Incoloy, Alloy Steel, Carbon Steel etc.						6	7	8	9			
	(2) Corrosion Mechanism Study								8	9			
VII	By-Product HCl Recycle									▲			
	(1) Reaction Kinetics with HCl						6	7	8	9			
	(2) Corrosion Measurement with HCl							7	8	9			
	(3) Data Evaluation								8	9			
VIII	Fluidization Mechanism Study												▲
	(1) Design and Install 4" Reactor								8	9	10		
	(2) Safety Review, Start-up									9	10		
	(3) Reaction Rate Measurements, Fluidized-Bed, Fixed-Bed										10	11	
	(4) Data Evaluation										10	11	
IX	Recommendations									▲			▲
	(1) Optimum Process Parameters									9			12
	(2) Optimum Material for Reactor									9			
	(3) Additional Development Work												12
	(4) Final Report												12

▲ Milestone Check Points

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July 22,1981.

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

(DRAWING NOT TO SCALE)

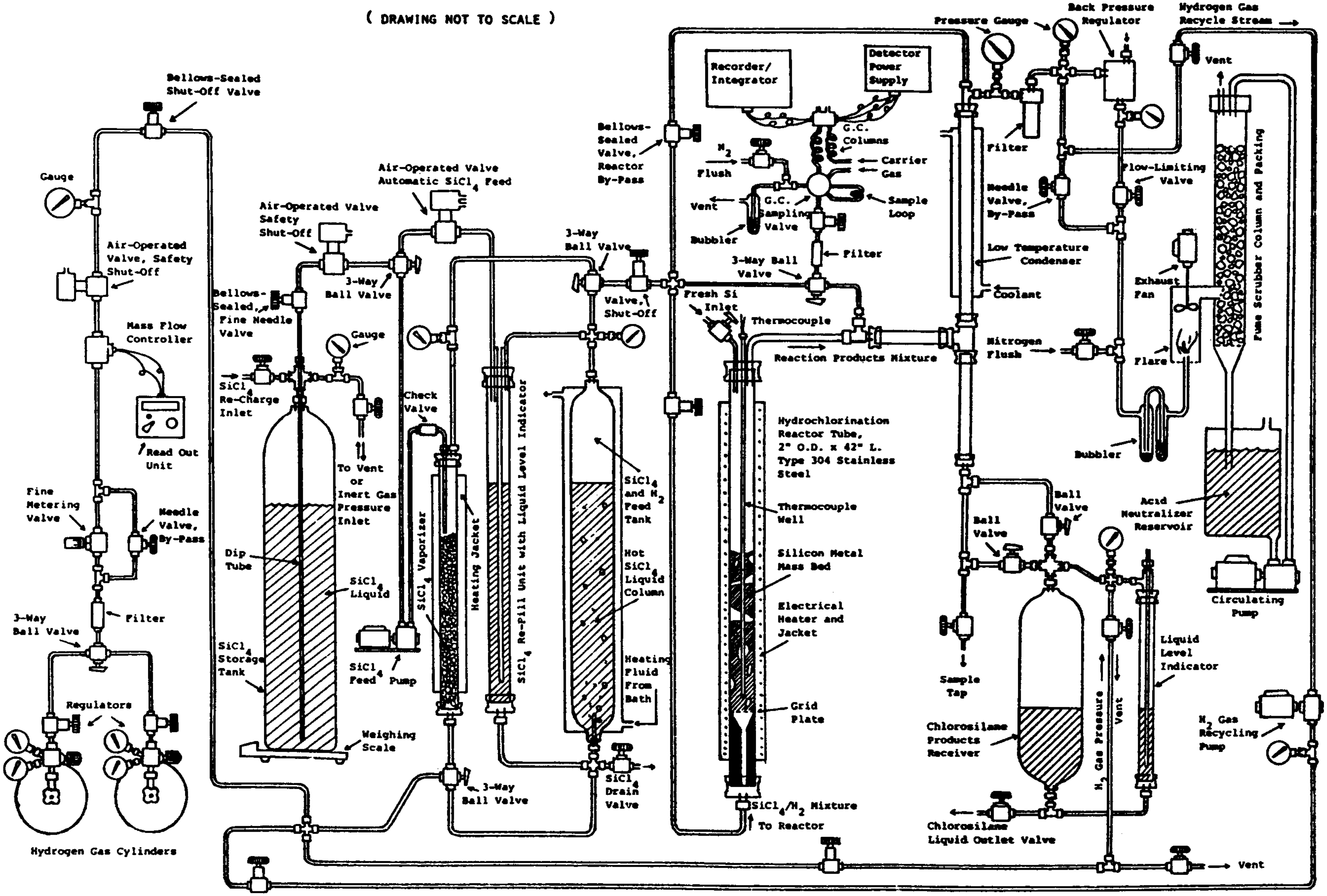

FIGURE II THE FLUIDIZED-BED REACTOR AND GRID DESIGN