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LOW-COST SOLAR ARRAY PROJECT: TASK I, SILICON MATERIAL

Investigation of the Hydrogenation of SiCl_4

Seventh Quarterly Report

By
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January 12, 1981

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LOW-COST SOLAR ARRAY PROJECT

TASK I SILICON MATERIAL

"Investigation of the Hydrogenation of SiCl_4 "

SEVENTH QUARTERLY REPORT

January 12, 1981

CONTRACT NO. 955382

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LOW-COST SOLAR ARRAY PROJECT

TASK I SILICON MATERIAL

"Investigation of the Hydrogenation of SiCl_4 "

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Department of Chemistry
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ABSTRACT

Experiments on the hydrochlorination of SiCl_4 and m.g. silicon metal to product SiHCl_3 were carried out with the object of studying the life of the silicon mass bed.

After 238 hours of reaction, no significant change in the reaction rate was observed. The longevity of the Si mass bed shows that the hydrochlorination process can be operated continuously for long periods of time without interruption. A material balance of 92.2% was made on silicon. These results confirm the stoichiometry of the hydrochlorination reaction as written in the above equation.

A corrosion study was made on Incoloy 800 as the selected material of construction for the hydrochlorination reactor in the Union Carbide EPSPDU. No measurable amounts of corrosion on this material were observed when a test sample was exposed to the hydrochlorination reaction for 238 hours at 500°C, 300 psig. A stable silicide protective film of approximately twenty microns thickness appears to form on the Incoloy 800 metal surface. However, this protective film is readily destroyed by air and moisture when it is exposed to the atmosphere. The serious corrosion problem as previously reported on the material of construction for the hydrochlorination reactor appear primarily due to atmospheric corrosion and not due to the reaction environment itself. As the present study indicates, Incoloy is a good choice as the material of construction for the hydrochlorination reactor.

INTRODUCTION

Research and development work on the JPL Contract No. 955 382 began in April of 1979 to study the hydrochlorination of SiCl_4 and m.g. silicon metal to SiHCl_3 . This Quarterly Report is the seventh in the series. Activities during this quarter include a series of experiments to study the life of the Si mass bed. The effect of prolonged reaction on the rate of the hydrochlorination reaction was studied. A material balance on the reaction was made. A corrosion study was made on Incoloy 800 as the selected material of construction for the hydrochlorination reactor in the Union Carbide EPSDU.

DISCUSSION

The laboratory scale stainless steel reactor for the hydrochlorination of SiCl_4 and m.g. silicon metal to SiHCl_3 is schematically shown in Figure I. The design and function of the hydrochlorination apparatus were reported in detail in the first Quarterly Report (DOE/JPL 955 382 - 79/1). The effect of impurities in the m.g. silicon metal on the reaction rate was last reported. During this quarter, a series of experiments was carried out to study the life of the silicon mass bed. The effect of prolonged reaction on the hydrochlorination reaction was studied. A test sample of Incoloy 800 was placed inside the reactor for corrosion measurements. Results are summarized in the following.

A. Mass Life Studies

A series of experiments was carried out to study the effect of prolonged reaction time on the hydrochlorination reaction. In practice, the hydrochlorination process must be able to sustain sufficiently long periods of operation before it has to be shut down for service. Thus, the longevity of the silicon mass bed is an important factor in operating the hydrochlorination process efficiently and economically.

The experiment was carried out at reactor pressure of 300 psig, a reaction temperature of 500°C and a $H_2/SiCl_4$ feed ratio of 2.0. Fresh Si metal was added intermittently to replenish the silicon metal consumed in the reaction. The reaction rate was monitored continuously by analyzing the composition of the reaction product mixtures at regular intervals of 2 to 4 hours.

After 238 hours of reaction, the experiment was terminated. Results of the reaction kinetic measurements are graphically presented in Figure II by plotting the % $SiHCl_3$ conversion versus residence time. The reaction rates fall within a range of 25 to 45 seconds residence time. The variable residence time is a result of the changing Si mass bed height. As Si metal is consumed by the hydrochlorination reaction, the residence time is shifted to a lower number. It moves back to a higher number when fresh Si metal is added to the reactor. As fresh Si metal is added from time to time during the course of the mass life study, the data points in Figure II move back and forth between 25 and 45 seconds of residence time. Although results in Figure II show some scattering of data points, the reaction rates are essentially constant within a narrow range throughout the 238 hours of reaction. The scattered data points are within the range of experimental error. Table I summarizes the results of some selected data points which have residence time which coincide with one another at about 32 seconds. As the results in Table I show, the hydrochlorination reaction rate remains constant throughout the 238 hours of reaction. Based on these reaction kinetic data, the Si mass bed appears to show a long mass life. The longevity of the Si mass bed is an important factor. It shows that the hydrochlorination process can be operated continuously for long periods of time without interruption.

B. Material Balance

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

A total of 46,659g (103 lbs) of chlorosilane product crude was collected during the course of the 238 hours of reaction. Analysis of the chlorosilane product mixture by gas-liquid partition chromatography showed the presence of 69 g of SiH_2Cl_2 and 7,944 g (17.5 lbs) of SiHCl_3 . The silicon consumption from these two chlorosilane products is calculated according to the above equation (1) for SiHCl_3 and equation (2) below for SiH_2Cl_2 ,

The total Si equivalent from 69 g of SiH_2Cl_2 and 7,944 g of SiHCl_3 products was calculated to give a total of 417.6 g 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 570 g m.g. silicon metal was charged into the reactor during the 238 hours of reaction. At the end of the experiments, 110.2 g of unreacted Si metal was recovered. Thus, $570 - 110.2 = 459.8$ g 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 is $459.8 \times 0.985 = 452.9$ g. 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 (1). As observed in previous experiments, the Si contents calculated from the chlorosilane products are generally lower than the value obtained from the difference between the spent Si mass bed and the total silicon metal charged. This may be explained by the fact that some volatile SiH_2Cl_2 (b.p. 8°C) and SiHCl_3 (b.p. 31°C) are lost by evaporation during handling and storage.

C. Corrosion Study

A piece of Incoloy 800 metal alloy was placed inside the hydrochlorination reactor for corrosion study during the course of the mass life study. This metal alloy has been selected as the material of construction for the hydrochlorination reactor in the Union Carbide EPSPDU, silane-to-silicon process. The Incoloy 800 test sample is schematically shown in the drawing in Figure III. It is cut from a piece of 1" O.D. x 1/16" wall tubing supplied by Union Carbide. The rings at the top and bottom of the middle strip are purposely constructed so as to hold the sample strip at the side wall inside the hydrochlorination reactor. The test sample was weighed (53.195 g) at the start of the experiment. After 238 hours of reaction, the sample was taken out and re-weighed: 53.520 g. Thus, there is a weight gain of $53.520 - 53.195 = 0.325$ g. A dense coating appears on the surface of the Incoloy 800 test sample. This coating has a physical appearance very similar to that obtained from the vapor phase deposition of Si with SiHCl_3 and H_2 at high temperatures. The test sample was measured to give a total surface area of 120 cm^2 . Assuming the deposited material is Si and the coating is uniformly distributed, the 0.325 g. represents a weight gain of 0.00271 g/cm^2 or a silicon metal film of about 11.6 microns (micrometers) thick. The fact that there

is no weight loss from the test sample indicates no significant amount of corrosion on the Incoloy 800 metal alloy.

After the Incoloy 800 test sample was re-weighed, it was immediately placed inside a Dry Box under an atmosphere of dry nitrogen. The middle strip (see Figure III) 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. Analysis of the surface coating on the Incoloy 800 metal alloy surface is in progress. To study the effect of atmospheric corrosion on the silicon coating, the bottom ring (see Figure III) was weighed (12.4025 g.). It was purposely exposed to air and moisture for a few days. As previously observed, the dense silicon coating on the Incoloy 800 test sample readily developed creeps and cracks. Pieces of the silicon 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 (12.1446 g). Thus, there is a weight loss of $12.4026 - 12.1445 = 0.2581$ g. 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 $0.00956 - 0.00271 = 0.00685 \text{ g/cm}^2$. In other words, some base metal from the Incoloy 800 test sample is also taken off along with the loosened scale. Taking the density of Incoloy 800 as 8.0 g/c.c. , about 8.6 microns of the base metal are removed from the metal surface with the silicon coating. These measurements provide evidence that the silicon deposited from the hydrochlorination reaction pene-

trates the Incoloy 800 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 800 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 Incoloy 800 test sample, a significant weight loss would be 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,

$$\text{Equilibrium Constant } K = \frac{(\text{SiHCl}_3)^4}{(\text{SiCl}_4)^3 (\text{H}_2)^2 (\text{Si})^0}$$

The activity of Si metal, $(\text{Si})^0 = 1$, 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 energetic Si atoms generated from the chemical reaction can diffuse into the metallic matrix to form the silicide protective film. As the reaction conditions fluctuate, the reversible reaction can shift in the opposite direction. Silicon in the silicide film is reacted away. As the activity of Si in the silicide film is reduced, silicon metal is re-deposited by the forward reaction. Thus, there is a dynamic equilibrium occurring at the surface of the reactor wall. 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.

Metal chlorides also are known to react with silicon metal,

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 (2). This is a plausible mechanism from which the metal reactor wall is protected from the highly corrosive HCl gas at elevated temperatures. Although present at much lower concentrations, metal chlorides, such as FeCl_3 , NiCl_2 and CrCl_3 can exist at the interface. The vapor pressure of these metal chlorides provides a driving force to remove these metallic elements from the reactor wall. On the other hand, the thermodynamically favored reactions (7), (8) and (9) provide the opposite driving force to keep these metallic elements on the reactor surface (as silicides). The high vapor pressure of titanium tetrachloride (b.p. 136°C) is the basis of an unstable Ti/Si silicide film since titanium in the silicide film constantly evaporates off as TiCl_4 . Thus, titanium metal is not suitable for the material of construction for the hydrochlorination reactor as previously reported by Union Carbide (Final Report, October 1975 - March 1979, JPL Contract 954 334). On the other hand, nickel and chromium produce the least volatile NiCl_2 and CrCl_3 among the chlorides of the conventional metals. Thus, silicides containing nickel and chromium form a stable protective film at the reactor wall as shown by the corrosion test for Incoloy 800 (40% Ni, 30% Cr, 30% Fe). Thus, these preliminary corrosion data show that Incoloy 800 is a good choice as the material of construction for the hydrochlorination reactor.

In conclusion, the corrosion test for Incoloy 800 produces 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 is insignificant. However, care should be taken to prevent atmospheric corrosion when the reactor is shut down for service or repair. The silicide protective film is readily destroyed

by air and moisture. The serious corrosion problems as previously reported by Union Carbide on their test results on Incoloy 800 and stainless steel are most likely due to atmospheric corrosion and not due to the hydrochlorination reaction environment itself.

D. Summary of Progress

Experimental work on the hydrochlorination of SiCl_4 and m.g. silicon metal to SiHCl_3 has progressed satisfactorily. Extra effort was placed on one mass life study (Item V B(1) in Program Plan) to include some important corrosion tests. This series of experiments has taken up more time than planned. No significant change in the reaction rate is noted after a prolonged reaction. The longevity of the Si mass bed in the hydrochlorination reactor is an important finding.

The corrosion test on Incoloy 800 produces 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 gas on conventional metals and alloys at temperature above 450°C are well-known. The presence of a protective silicide film at the reactor wall eliminates this potential corrosion problem.

PROJECTED EIGHTH QUARTER ACTIVITIES

Planned activities for the final quarter (January - March) of the JPL Contract No. 955 382 include,

- Analysis on corrosion test sample
- Analysis on spent Si mass bed and elutriated fines
- Mass life studies
- Other hydrogenation catalysts
- Final Report

LSA PROJECT SILICON MATERIAL

TABLE I HYDROCHLORINATION OF SiCl_4 AND M.G. SI AT 500°C , 300 PSIG AND $\text{H}_2/\text{SiCl}_4 = 2.0$

EXPERIMENT DATE	CUMULATIVE REACTION TIME HOUR	SILICON MASS BED G.	HYDROGEN FEEDRATE SCCM	RESIDENCE TIME SECOND	SiH_2Cl_2 MOLE %	SiHCl_3 MOLE %
8/28/80	25	151.7	1340	31.2	0.4084	22.30
9/10/80	65	136.4	1146	32.8	0.3641	22.53
10/20/80	155	126.3	1070	32.5	0.4809	22.10
10/28/80	183	129.8	1080	33.1	0.4049	21.87
11/7/80	229	129.5	1090	32.7	0.4357	22.35

FIGURE 1 Apparatus For The Hydrogenation Of SiCl_4 To SiHCl_3

FIGURE II

PROLONGED HYDROCHLORINATION
REACTION OF SiCl_4 AND m.g. SILICON
AT 500°C , 300 PSIG, $\text{H}_2/\text{SiCl}_4 = 2.0$

FIGURE III

INCOLOY 800 TEST SAMPLE

Year	Month of Year	Month of Contract
I Program Plan, Laboratory Site Preparation		
II Finalize Reactor Design, Order Equipment		
III Construct Hydrogenation Apparatus		
IV Safety Review, Start-Up, Standardization		
V Process Studies		
A. Reaction Kinetics		
(1) Function of T,P,H ₂ /SiCl ₄ with no Catalyst		
(2) Establish Rate Equation, Reaction Order		
(3) Copper Catalyst Studies: T,P,H ₂ /SiCl ₄		
(4) Particle Size Distribution, Surface Area		
(5) Different Grade of MG Si		
B. Mass Life Studies		
(1) With no Catalyst Added		
(2) With Cu Catalyst Added		
(3) Different Grade of MG Si		
VI Research and Development		
A. Method of Preparing Cu/Si Mass		
(1) Literature Studies		
(2) Prepare Cu/Si Mass		
(3) Evaluation and Optimization		
B. Reaction Mechanism Studies		
(1) Literature Studies		
(2) Identify Reaction Intermediates: HCl, etc.		
(3) Identify Intermediate Reaction Steps		
(4) Nature of the Equilibrium Reactions		
(5) The Role of Copper Catalyst		
a. Nature of the Catalytic Sites		
b. Copper Transport Mechanism		
c. Copper Distribution on Solid Si Surfaces		
(6) Kinetic Isotope Effect		
C. Other Hydrogenation Catalysts		
VII Reports		
A. Recommendation on Optimum Reaction Conditions		
B. Recommendation for Additional Development Work		
C. Final Report		

▲ Milestone Check Points