

**RECOVERY OF VALUABLE CHLOROSILANE
INTERMEDIATES BY A NOVEL WASTE
CONVERSION PROCESS**

**Final Technical Report
July 1994 - September 2001**

By

J. Ashley Brinson

December 2001

Work Performed Under Cooperative Agreement
No. DE-FC04-94AL99566

For
U.S. Department of Energy
Office of Industrial Technologies (EE-20)
Washington, DC

By
Dow Coming Corporation
Midland, Michigan

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ABSTRACT

From 1994 to 2001, Dow Corning studied a waste recycling process to recover direct process residues (DPR) resulting from the production of silicone precursors. Over the course of eight years, Dow Corning constructed and operated a pilot plant, a small scale commercial plant, and a full scale plant. The process reacts DPR with hydrogen and chlorosilane monomers at high temperature and high pressure. The process converted 85% of the DPR to valuable chlorosilane monomers such as dimethyldichlorosilane and methyldichlorosilane. When feeding methyltrichlorosilane, the process converted 30% of the MeSiCl_3 to other monomers. Alternate co-feed monomers were tested. By converting waste DPR to valuable intermediates, the technology significantly reduces waste from the basic silicones manufacturing process.

PREFACE

This report documents the final results of the project "Recovery of Valuable Chlorosilane Intermediates by a Novel Waste Conversion Process", Cooperative Agreement number DE-FC04-94AL99566. The objective of this Dow Corning Corporation (DCC) and U.S. Department of Energy (DOE) cost-shared project was to develop a process for recycling waste residues from the basic silicones production process. The project started with Phase IIIA, Engineering development - Intermediate Scale, which consisted of testing with two systems, termed the Pilot Plant and Pilot Plant II, both at Carrollton, Kentucky. Phase IIIB, Engineering Development - Full Scale, was the development of the full scale commercial system at Barry, Wales, UK. Further details of the work are provided in technical annual reports DOE/AL/99566-1, DOE/AL/99566-2, and DOE/AL/99566-3.

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Brian Valentine is the Program Manager in the DOE Office of Industrial Technologies. Robert Lowther is presently the Contracting Officer for the DOE Albuquerque Operations Office. Ken Lucien is the Project Manager for the DOE Albuquerque Operations Office. Steve Freeburne is the Dow Corning Corporation Director of Science and Technology for the Core Products Business. Ollie Wilding is the DCC Methyl Intermediates Technology Center Manager. Clay Chagot is the present DCC Contracts Specialist for the project. Darrell Whiteley and Kurt Anderson were past Principal Investigators. Stuart Bolland is the Start Up Coordinator for the process in Barry. Christine Stump and Scott Nab are the Manufacturing Engineers responsible for the daily operation of the Carrollton unit. Ashley Brinson is the Principal Investigator and author of this report.

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TABLE OF CONTENTS

1.0 INTRODUCTION.....	1
1.1 SILICONES	1
1.2 CHEMISTRY.....	1
1.3 THE DIRECT PROCESS CHEMISTRY.....	3
1.4 DPR COMPOSITION.....	4
1.5 THE DPR WASTE PROBLEM.....	5
1.6 OBJECTIVES OF THE PROJECT.....	5
2.0 BACKGROUND.....	7
2.1 LABORATORY SCALE (1989-1994).....	7
2.2 BEGINNING OF DEPARTMENT OF ENERGY SUPPORT (1994).....	8
3.0 PROJECT CHRONOLOGY.....	9
3.1 PILOT PLANT (1994-1996).....	9
3.2 INTERMEDIATE SCALE (1997-PRESENT).....	13
3.3 FULL SCALE (1997-PRESENT).....	16
4.0 ENERGY AND WASTE BENEFITS.....	21
4.1 BASIS OF ANALYSIS.....	21
4.2 MAGNITUDE OF THE DPR WASTE PROBLEM.....	21
4.3 CURRENT VS. PROPOSED TECHNOLOGY.....	22
4.4 MARKET PENETRATION.....	23
4.5 ENERGY AND WASTE SAVINGS.....	23
5.0 BUSINESS CONSIDERATIONS.....	27
5.1 ECONOMIC ATTRACTIVENESS.....	27
5.2 POLICY/REGULATORY.....	30
5.3 INDUSTRIAL COMPETITIVENESS.....	30
5.4 COMMERCIALIZATION PLANS.....	30
5.5 FOREIGN TRADE.....	31
6.0 SUMMARY.....	32
7.0 REFERENCES.....	33
APPENDIX 1.....	A-0

Index of Figures

FIGURE 1: FLOW DIAGRAM FOR SILICON MANUFACTURING PROCESS	2
FIGURE 2: FLOW DIAGRAM FOR DIMETHYLDICHLOROSILANE PRODUCTION VIA THE DIRECT PROCESS	3
FIGURE 3: FLOW DIAGRAM FOR DPR HYDROGENOLYSIS TECHNOLOGY.....	8
FIGURE 4: ECONOMIC SENSITIVITY TO PLANT SIZE	29
FIGURE 5: ECONOMIC SENSITIVITY TO Me_2SiCl_2 PRICE	29

Index of Tables

TABLE 1: DIRECT PROCESS PRODUCT DISTRIBUTION	4
TABLE 2: DPR COMPOSITION	4
TABLE 3: ENERGY USAGE FOR THE MANUFACTURE OF SILICON	24
TABLE 4: ENERGY SAVINGS	25
TABLE 5: WASTE REDUCTION	26
TABLE 6: ECONOMIC COMPARISON OF DPR DISPOSAL ALTERNATIVES	28

RECOVERY OF VALUABLE CHLOROSILANE INTERMEDIATES BY A NOVEL WASTE CONVERSION PROCESS

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1.0 INTRODUCTION

1.1 Silicones

Silicones are a versatile family of man-made polymer materials used in numerous industrial and consumer applications. Silicone fluids are used in cosmetics, power transformers, automobile brake hydraulics, and industrial heat transfer systems. Silicone rubbers are used for high performance industrial and military applications that require superior electrical insulation properties, weather resistance, stability, and nontoxicity. Products as diverse as bathtub caulk, medical tubing, electronic encapsulants, and engine gaskets are based on silicone rubber formulations.

In 1998, Chemical Economics Handbook (CEH) Marketing Research estimated the total global silicones market at a volume of \$6.7 billion.¹ Global production is dominated by the American manufacturers Dow Corning and General Electric, who account for approximately 50% of the global market share.² Growth of silicones is approximately 6% per year.³ Major new production plants were constructed in the 1990's, and further expansions are expected in future.

1.2 Chemistry

The starting point for silicones is chemical grade silicon metal. (Although the exact smelting process chemical reaction steps are subject to some expert disagreement, the process can be generalized for purposes here.) The silicon is smelted from quartz (SiO_2) in a submerged arc furnace through a series of carbothermic reducing reactions that produce silicon monoxide (SiO) and silicon carbide (SiC) as principal intermediates. These, in turn, react to yield silicon metal and carbon monoxide (CO). Coal, coke, and dry wood are added for carbon sources. The process uses large amounts of energy, and most of the manufacturing cost of the silicon is the energy cost. A typical process is shown in Figure 1 on the following page, from the text of Schei, Tuset, and Tveit.⁴

¹ Smart, p. 5.

² Ibid.

³ Ibid.

⁴ Schei et al., p. 15.

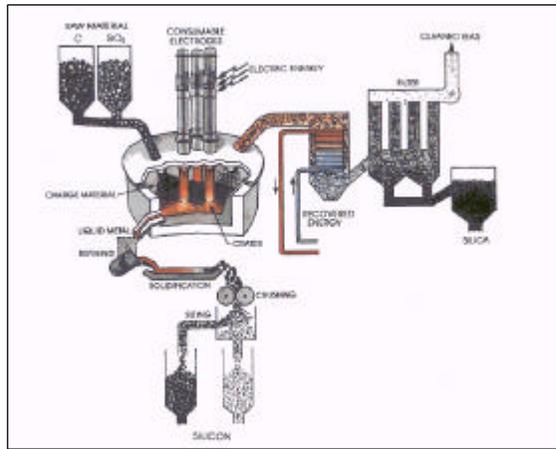


Figure 1: Flow Diagram for Silicon Manufacturing Process

The overall reduction reaction for the silicon manufacturing process is: $\text{SiO}_2 + 2 \text{C} \rightarrow \text{Si} + 2 \text{CO}$

The next step in the manufacture of silicones is the production of dimethyldichlorosilane (Me_2SiCl_2) where "Me" is the methyl organic group $-\text{CH}_3$. Me_2SiCl_2 is made from the reaction of methyl chloride and silicon metal in a system known as the "direct process". A typical process is shown in Figure 2 on the following page.⁵ The bulk silicon is ground to a fine powder and fed to a fluidized bed reactor (FBR) with methyl chloride gas. The direct process reaction occurs at approximately 300 °C. It is catalyzed and promoted with various additives. The various methylchlorosilane products and byproducts are then separated by distillation.

⁵ Mark, p. 521.

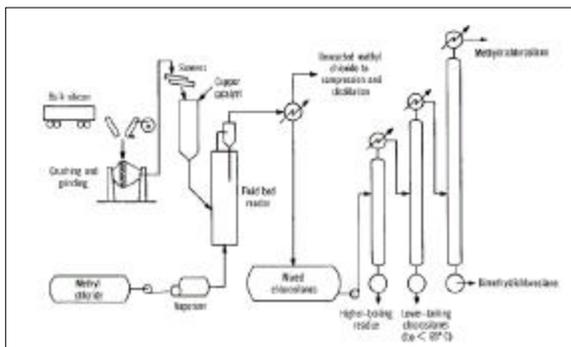
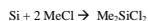
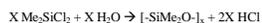


Figure 2: Flow Diagram for Dimethyldichlorosilane Production via the Direct Process

The main desired chemical reaction of the direct process is:



Silicone polymers are then produced by hydrolysis of the Me_2SiCl_2 .



1.3 The Direct Process Chemistry

Although Me_2SiCl_2 is the main desired product, several other chlorosilane monomers and oligomers are produced in side reactions. The byproduct monomers include methyltrichlorosilane (MeSiCl_3), trimethylchlorosilane (Me_3SiCl), methyldichlorosilane (MeHSiCl_2) and lesser amounts of other monomers. The oligomers include a high boiling mixture of disilanes, silmethylenes, and polysilalkylenes known as "direct process residue" or DPR. All major manufacturers operate a similar process to produce crude chlorosilanes. A typical product distribution is shown in Table 1 on the following page, from Ullmann's Encyclopedia.⁶

⁶ Ullmann's, Volume A-24, p. 25.

Table 1: Direct Process Product Distribution

Specie	Range [weight percent]
Me ₂ SiCl ₂	70%-90%
MeSiCl ₃	5%-15%
Me ₃ SiCl	2%-4%
MeHSiCl ₂	1%-4%
Me ₂ HSiCl	0.1-0.5%
DPR	3%-8%

The temperature, catalysts, and raw materials purities are optimized and tightly controlled to maximize the selectivity towards desirable Me₂SiCl₂, and to minimize the production of less valuable monomers and DPR.⁷ The minor monomers, Me₃SiCl and MeHSiCl₂, are valuable, though their demand in the marketplace fluctuates. Me₂HSiCl is presently highly valuable as an intermediate to certain expensive organosilanes. MeSiCl₃ has only limited value, and DPR is essentially a waste. Despite attempts to minimize its formation, some level of DPR production always occurs.

1.4 DPR Composition

DPR consists of disilanes, silmethylenes and polysilalkylenes. Disilanes are those species with two silicon atoms directly connected. Such a disilane specie is 1,1,2-trichloro-trimethyldisilane, MeCl₂SiSiMe₂Cl. Silmethylenes are similar molecules, but the silicon atoms contain the methylene group, -CH₂-, between the silicon atoms. Such a silmethylene specie is MeCl₂SiCH₂SiMe₂Cl. Higher molecular weight species are generically referred to as "high boilers" because their boiling points are above the disilanes and silmethylenes. They are also called polysilalkylenes.

A typical DPR composition is given below.⁸

Table 2: DPR Composition

Specie	Range [weight percent]
Disilanes	30%-80%
Silmethylenes	5%-30%
High Boilers	10%-40%

⁷ Koerner, p. 7.

⁸ Ferguson et al., US Patent 5,430,168

1.5 The DPR Waste Problem

DPR losses have been estimated to cost 4% to 8% of the total raw material cost for dimethylchlorosilane.⁹ Direct process residue can be handled in several ways, and different silicone manufacturers practice different waste disposal technologies.

One disposal method for DPR waste is incineration.¹⁰ To minimize formation of dioxins, incineration temperatures for chlorinated organics are high, and residence times are long. Incinerators are highly regulated by government environment agencies, and public concern for incinerator emissions is elevated. Regulations have increased, and modern incinerators are expensive capital investments. Chloride value can be recovered from the combustion products (by absorption) to produce aqueous HCl that is recycled to produce MeCl, but this is also an expensive capital investment. Recovery of waste heat is another option to improve incineration as an environmentally responsible alternative, but heat recovery is difficult due to silica dust in the combustion off-gas. Fine silica particulates require expensive flue gas scrubbers. After incineration, the silica solid must be disposed, typically by landfill.

Another disposal method for DPR waste is hydrolysis. DPR is hydrolyzed (or "quenched") with water to form a solid byproduct.^{11, 12} An alkali, such as lime slurry, is added to neutralize the hydrochloric acid formed by hydrolysis. This forms solid gels that are suitable for landfill disposal. This process avoids incineration, but does not recover the chloride value or the silicon value of the raw materials. This sort of a quench process is relatively simple and requires low capital investment.

Finally, disilanes can be distilled from the higher boiling species and reacted to yield monomers. Disilanes can be reacted with hydrogen, HCl, or chlorine in a catalytic or thermal cracking process.¹³ Although this technology is mature, it has two serious problems. First, it only handles a portion of the DPR stream. Prior to 1994, no process had been demonstrated to handle the entire DPR stream. Since 40% of the DPR is dimethylsilanes and higher boilers, and since these cannot be recovered, disilane cracking must be practiced with incineration or hydrolysis. Second, the product from disilane cracking is a mixture of low value monomers rich in MeSiCl₃. Converting DPR to MeSiCl₃ worsens the oversupply of this low value monomer. Thus the cracking of disilanes is of limited utility to solve the DPR waste problem.

1.6 Objectives of the Project

The objectives of this project were to scale up a process to recycle DPR internally within the silicones manufacturing plant and to produce a high value product. Such a process offers significant economical

⁹ Freeburne, *Silicon for the Chemical Industry III*, p. 303.

¹⁰ Coleman and Tambo.

¹¹ Breneman and Reeser.

¹² White et al.

¹³ Freeburne, *Silicon for the Chemical Industry III*, p. 304.

advantages over the existing waste disposal and recovery processing technologies. The benefits to Dow Corning are superior environmental performance (reduced landfill waste, reduced waste treatment costs), raw material conservation (recovered chloride and silicon costs), and valuable monomer production. Because silicon manufacture is an energy intensive process, landfill disposal alternatives result in high energy waste. Thus, DPR recycling also meets the Department of Energy objective to reduce energy usage.

The specific targets of this project were:

- Demonstrate DPR conversion at 85%.
- Demonstrate MeSiCl₃ conversion at 30%.
- Demonstrate high value product.
- Demonstrate reliable operation with high on-line time and low rate of mechanical breakdowns.
- Demonstrate DPR hydrogenolysis technology at a commercial scale.

2.0 **BACKGROUND**

2.1 **Laboratory scale (1989-1994)**

Prior to this project, Dow Corning operated laboratory scale reactors to screen potential DPR reactions and demonstrate viable DPR conversion chemistry. These reactors were the basis for early patent activity on DPR hydrogenolysis in 1989 to 1994. This laboratory research resulted in the publication of five US patents prior to commencement of the project.^{14, 15, 16, 17, 18}

A significant breakthrough came when researchers discovered the process for reacting MeSiCl₃, DPR, and H₂ with an in-situ catalyst present in the DPR.¹⁹ The catalyst was identified as aluminum chloride, AlCl₃, which is formed in the direct process from the reaction of aluminum with chlorine species. The aluminum is present in the silicon raw material. The aluminum chloride catalyst is superior in its performance, and unlike expensive palladium and platinum catalysts previously studied, it is absolutely free. The high pressure hydrogenation resulted in 99% conversion of disilanes, 55% conversion of silylmethylenes, and 71% conversion of polysilylalkylenes. The overall DPR conversion was 91%, far superior to the 60% recovery previously practiced for disilane cracking technology. Additionally, MeSiCl₃ co-feed resulted in a 19% to 30% net consumption of the MeSiCl₃, and conversion to other useful products, including Me₂SiCl₂. This was also a significant improvement in prior disilane cracking technology. US Patent 5,430,168¹⁹ was issued to Ferguson, Naasz, Oltmanns, Warrick and Whiteley on July 4, 1995.

The basic process is shown as Figure 3 in the block diagram on the following page:

¹⁴ Chadwick et al., US Patent 5,292,909.

¹⁵ Chadwick et al., US Patent 5,292,912.

¹⁶ Chadwick et al., US Patent 5,321,147.

¹⁷ Chadwick et al., US Patent 5,326,896.

¹⁸ Bokerman et al., US Patent 5,175,329.

¹⁹ Ferguson et al., US Patent 5,430,168.

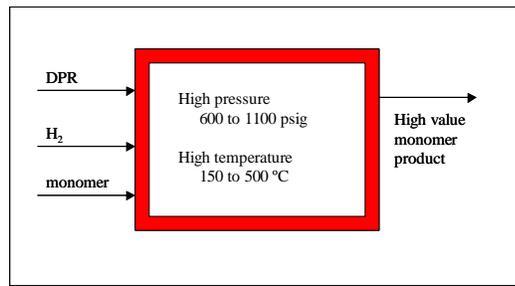


Figure 3: Flow Diagram for DPR Hydrogenolysis Technology

2.2 Beginning of Department of Energy Support (1994)

Although the laboratory work appeared promising in 1993, the DPR hydrogenolysis technology still presented significant technical and commercial risks. A substantial scale-up was required to demonstrate the chemistry on a full-scale process. Outstanding issues regarding fundamental chemistry and chemical engineering required a high level of technical support to resolve. The novelty of high pressure reaction with highly flammable hydrogen gas also presented challenges to the engineers, since most processes in the basic silicones plant operate only slightly higher than ambient pressure.

To mitigate the technical and financial risks and to accelerate the desired ultimate technology commercialization, Dow Corning solicited support from the Department of Energy. A cost sharing arrangement was established so that less than 10% of the project's total costs would be borne by the DOE. The form of support was mainly reimbursement for the expense of start-up engineers, with capital costs absorbed by Dow Corning.

3.0 PROJECT CHRONOLOGY

3.1 Pilot Plant (1994-1996)

The first phase of DOE supported work was the pilot plant. The objective of this phase of work was to build and operate a pilot reactor based upon the successful laboratory reactor, but approximately 500 times larger (as measured in process throughput). The pilot plant was erected in Carrolton, Kentucky. Process development engineers from the Silicon and Methyl Intermediates Department designed the reactor and eventually operated it. A separate team of engineers from the Capital Projects Department purchased the equipment and issued the construction work packages to fabricate and assemble the plant. The plant was constructed in 1994 and operated until 1996. The process was manned with engineers 24 hours per day to achieve continuous operation. The goal of this work was to demonstrate the feasibility of DPR hydrogenolysis at a plant size approaching commercial scale. Important technological lessons from this plant led to changes in product recovery, reactor selection, and materials of construction in subsequent phases of the project.

3.1.1 Pilot Plant Detailed Design

In the first half of 1994, detailed design of the small pilot plant began. A Process Flow Diagram (PFD) was created for the pilot plant with material and heat balances. Next, Piping and Instrumentation Diagrams (P&IDs) were drawn. All the pilot plant equipment was designed and specified. A Hazards and Operability Study (HAZOP) was undertaken to analyze and improve the safety of the plant. Necessary state construction permits were obtained. Vessels, pumps, and instrumentation devices were purchased. The construction contract was awarded to a 'local' company to build the pilot plant on skids in a fabrication facility about fifty miles away from the Carrolton site. These skids were then shipped to the site and anchored to the floor in the pilot plant process tower.

3.1.2 Pilot Plant Construction

The first skids arrived on site in October of 1994. Approximately 80% of the piping was complete when the skids arrived. The remaining piping was installed with the equipment in place. In November, the instrumentation package was installed and tested. Insulation and heat tracing was installed. In December, process tie-ins were completed to transfer feeds to the pilot plant, and the integrated process was pressure tested. Final safety audits were completed, standard operating procedures were written, and final minor modifications were made.

Successful pressure testing proved to be a difficult task. Due to the relatively high operating pressure and the hazardous nature of the chemicals involved, it was imperative to have great confidence in the mechanical integrity and containment of the plant. Lack of experience in the

design of high pressure systems resulted in several minor problems in the initial design and construction of the facility. Although the issues were individually minor, they resulted in numerous leaks that were discovered during pressure testing. New procedures were then developed for systematically locating these tiny leaks, and new design and construction techniques were developed to repair them. Many of these procedures were completely new to Dow Coming. Pressure testing eventually took three months to complete, but the effort was very valuable. Refining the design standards and construction techniques at this early stage proved to be prudent in the long run, as during the life of the small pilot plant, there were no leaks of hazardous fluid due to fundamental pipe design or installation errors.

3.1.3 Pilot Plant Commissioning

The first commissioning activities began in February, 1995. The hot oil system was started up, and shortly thereafter, it was discovered that the heater was undersized. A new heater was ordered, but this resulted in a delay of about six weeks. Additional problems were discovered in the low pressure valves. These were corrected, and the commissioning of the oil system was completed in April.

Chemicals were first introduced to the unit in April of 1995. DPR was filtered in the pilot plant prior to introduction to the reactor. The first high pressure feed to the reactor was initiated with a two day experiment in May, 1995. By this time, all commissioning activities were completed.

3.1.4 Pilot Plant Operational Studies and Optimization

The first two experiments were conducted in June, 1995. During these initial experiments, DPR conversion was approximately 75%. Methyltrichlorosilane conversion ranged from 27% to 33%. Feed rates approached the design basis for the pilot plant. These results were very close to the project targets.

However, a significant problem was experienced in the second experiment. The product recovery system became plugged. Process modifications made to overcome the plugging problem yielded mixed results. Further modifications were made in July and August, but resolution of the product recovery plugging problem proved to be a difficult technical issue. The pilot plant continued running in short campaigns to test various modified process configurations intended to overcome the plugging of the product recovery unit.

During the tests of different product recovery systems, the plant equipment was repeatedly disassembled and reassembled. This allowed atmospheric moisture to enter the system, which subsequently contributed to a slight acid attack on the materials of construction. This mild acid corrosion was aggravated by the operating conditions of high pressure and temperature and by the

presence of hydrogen. Three failures of piping components were eventually discovered in areas of high mechanical stress. The mode of corrosive failure in chlorosilane service was known by Dow Corning, but was not expected in this system. Various experts in metallurgy were consulted to review the failures. The pilot plant team created new corrective action plans and management plans to mitigate the risk of catastrophic piping failure due to this corrosion mechanism. Test coupons were installed to study the process and to select materials for later plant scale-up.

In September of 1995, another significant setback was experienced. Solid polymers were discovered in the reactor vessel itself. These deposits plugged the reactor and prevented operation of the pilot plant. The solids could not be dissolved, and the system was shut down for cleaning.

Due to the significant problems experienced through October of 1995, the project engineers decided that a fundamentally different reactor and product recovery design would be required for the full scale plant. With due consideration of the technical risks associated with a large scale-up in the face of the issues then unresolved, an intermediate scale-up step was proposed and accepted. Accordingly, the project team was split into two groups. One group began design of an intermediate scale system. The second group worked on cleaning the plugged pilot reactor and modifying the pilot system so that it could be operated in the interim period until the intermediate scale system could be designed and constructed.

From November of 1995 to January of 1996, numerous changes were made to the pilot plant to improve reactor mixing and to test new product recovery technology. Shift work resumed in January, and the pilot plant was restarted to test the design changes. Additional changes were made to test the effect of feeding new monomers with DPR. Some test reactions were made in the laboratory. Further laboratory work analyzed the reactor solids to learn more about the reaction mechanisms that caused the solids formation.

In February of 1996, two successful campaigns were completed. High DPR conversion was achieved, and product distributions were very favorable. The new monomer feed modes proved to have significant and unexpected benefits for product distribution.²⁰ Additional laboratory work confirmed and extended the results. Eventually, three additional patents were filed in the area of

²⁰ Brinson et al., US Patent 5,606,090.

DPR hydrogenolysis,^{21, 22, 23} and four more patents were filed in related areas of DPR conversion chemistry.^{24, 25, 26, 27} Further campaigns in March yielded record high conversion of 86% and progressively longer periods of sustained operation between shutdowns. Product recovery plugging was solved with the modifications made in the late autumn/early winter redesign. The significant challenge remaining was polymerization in the reactor itself.

In April 1996, the pilot plant was shut down due to planned maintenance in the adjacent commercial FBR plant. The opportunity was taken to inspect the reactor vessel for corrosion and to remove and inspect various corrosion coupons. At that time, a significant crack was discovered in the reactor head. The crack was repaired, and plans were made for a final campaign. In May, several attempts were made to restart the pilot plant, but these were abandoned when the feed pump failed. This was the final attempt to operate the pilot plant. Several feed tanks were removed from the tower and reinstalled for use on the intermediate scale plant. In the summer of 1997, the pilot plant was decommissioned. Equipment remaining after salvage was demolished or abandoned in-situ in a safe state.

3.1.5 Pilot Plant Results

The final results of the pilot plant operation were as follows:

- DPR was converted at up to 86% efficiency.
- MeSiCl₃ was converted at up to 33% efficiency.
- High value product was consistently recovered. New monomer feed technology was demonstrated.
- Reaction conditions and side reactions were studied in the laboratory and pilot plant.
- DPR filtration was demonstrated.
- Product separation and recovery were optimized. Product recovery problems were overcome.
- Capacity testing was completed.

Significant technical questions and problems remained:

- Reliability was generally poor; the longest pilot plant campaign was just over three days.
- Several areas of the plant suffered corrosive failures.
- Polymerization in the reactor created stubborn plugging that shut down the process and limited operating time.

²¹ Brinson et al., US Patent 5,606,090.

²² Freeburne et al., US Patent 5,627,298

²³ Freeburne et al., US Patent 5,629,438.

²⁴ Brinson et al., US Patent 6,013,255.

²⁵ Crum et al., US Patent 5,907,050.

²⁶ Crum and Wood, US Patent 5,922,894.

3.1.6 Pilot Plant Commercialization Plan

The pilot plant results demonstrated that the fundamental reaction chemistry worked at a scale approximately 500 times larger than the laboratory reactor. However, significant problems were discovered with product recovery, corrosion, and reactor solids. These problems presented sufficient technical uncertainties that the commercialization plan was significantly changed. By October of 1995, it was judged imprudent to scale up immediately to a full sized commercial plant. An intermediate scale design was proposed by project engineers. Preliminary designs and estimates for this plant began in late 1995.

The modified commercialization plan was supported by company management and proposed to the Department of Energy. The Statement of Work and Cost Plan were updated.

3.2 Intermediate Scale (1997-present)

The intermediate scale process has previously been described as an intermediate scale commercial reactor and a large pilot plant. In reality, it is both. The reactor is integrated with a small, but fully operational basic methyl chlorosilane production plant in Carrollton, Kentucky. This unit is the oldest and smallest of three commercial processes operating at the site. Installation of the DPR hydrogenolysis reactor allowed the technology to be tested in a small plant without risking larger business assets due to problems with quality or reliability.

The reactor started up in October, 1997, and continues to operate today. Several modifications have been made to the system to increase capacity and allow the same process to react significantly higher amounts of DPR.

3.2.1 Intermediate Scale Process Design

Part time design on the intermediate scale process began in late 1995. In October of that year, a preliminary technology package was written. The design was reviewed with manufacturing personnel, finalized in December, and presented to a contract engineering firm in January 1996. Piping and instrumentation diagrams were completed in December, 1995, and HAZOP studies were completed in January, 1996. Equipment was specified and ordered. Plant layouts were developed.

3.2.2 Intermediate Scale Detailed Design and Procurement

In February, 1996, the completed preliminary design package was issued for detailed design. The project was executed on a "fast track" schedule. By early May, all the major equipment was on

²⁷ Wood, US Patent 6,013,824.

order, and the critical path was determined to be delivery of the reactor. A larger volume hydrogen supply contract was executed in August.

3.2.3 Intermediate Scale Construction

The first construction packages were issued in June 1996. The filter area process tower modifications were completed in July, and the reactor area steel structure was completed in November. By the end of 1996, all equipment had been received at the site except for the reactor vessel. The new hydrogen supply and the reactor were both installed in January, 1997.

3.2.4 Intermediate Scale Commissioning

A start-up team was assigned in December, 1996. Training for the engineers was completed by January, 1997. Standard operating procedures were written by the startup engineers. Although supported by engineers, this plant was operated by the regular technicians from the manufacturing plant. Plant technician training was completed in April, 1997.

Due to the long procurement time for the reactor, sub-systems were started up in sequential order. The first system started up was the filter, which was commissioned in April, 1997. The oil heating system was commissioned one month later. Several problems were discovered with high pressure piping components. Among these, the worst problem was leaking valves. This situation was discovered in May of 1997, but not ultimately resolved until September. The first feeds to the reactor commenced in early October, 1997.

3.2.5 Intermediate Scale Operation and Optimization

The start up engineers supported the intermediate scale operation through July, 1998. During this time, several campaigns and experiments were conducted. Reaction temperature was decreased from the pilot plant to the intermediate scale, a permanent operating change to reduce solids formation which did not reduce DPR consumption. Low hydrogen feed was tested, but did not work well. During certain low hydrogen experiments, DPR conversion fell to as low as 30%. The optimum hydrogen feed rate was determined. Hydrogen conversion was measured in several experiments, as was conversion of disilanes and various DPR species to hydrogenated Si-H species.

The ratio of monomer to DPR feed was varied to test the effects. Results were analyzed, but the effects were difficult to measure directly. Sampling the high pressure system was difficult and hazardous. Online analysis of product distribution was feasible, but very difficult. Long term analysis of the train monomer output was used to determine DPR conversion and product composition. Broad optimum ranges of monomer feed ratios were defined.

The amount of in-situ catalyst necessary was measured and optimized. Various operating strategies were tested. The limits of minimum catalyst were determined by co-feeding distilled dislanes without catalyst to see at what level the reactivity was lost. Operating strategies were developed to maximize overall DPR waste consumption.

Reactor residence times were calculated. Feed rate trials were conducted to test various sub-systems and determine their capacity. Heat transfer was studied, and energy inputs and outputs were calculated or estimated. Thermal losses and heats of reaction were calculated. Heat transfer coefficients were calculated for various heat exchangers and the reactor heat transfer area.

The mode of product recovery from the reactor was optimized, and reactor fluid was withdrawn in various physical phases. Through several experiments and several months of optimization, a superior mode of product removal was developed. Through this effort, a mode of operation was discovered that eliminated solids plugging downstream of the reactor in transfer piping and distillation equipment. This was a serious concern unresolved from the pilot plant. The new modes of operation and new automation/control strategies eliminated this problem in the intermediate scale system.

3.2.6 Intermediate Scale Results

During the time period of October of 1997 to July of 1998, DPR conversions of 60% to >90% were achieved for sustained periods of operation. Various system parameters were optimized. The start-up team was disbanded, and the process was handed over to normal plant operating personnel.

The final results of the intermediate scale operation were as follows:

- DPR was converted at greater than 90% efficiency for sustained campaigns.
- High value product was consistently recovered.
- Small scale commercial operation was demonstrated.
- Integration of the technology with an entire basic process train was achieved.
- Reliability was greatly improved compared to the pilot plant.
- Polymerization was greatly improved compared to the pilot plant.
- Corrosion mechanisms were understood and controlled.

3.2.7 Intermediate Scale Commercialization Plan

Subsequent to the original scope of work for this cooperative project, the entire Carrollton intermediate scale DPR conversion system was modified and "stretched" so that its capacity now significantly exceeds the original design feed rates. The plant is still operating to recycle as much

waste as possible, and it provides a very significant benefit to the entire Carrollton, Kentucky, operation.

There are still several challenges and operating difficulties for the intermediate scale reactor. Compared to other chlorosilane processes on site, the ongoing maintenance costs are comparatively expensive, and although it is improving, mechanical reliability is still below desired levels. The process still requires full time assignment of one engineer to maintain reliable operation. Solids formation in the reactor continues to be problematic, but incidents of serious plugging are gradually fewer as learning increases and better modes of operation are implemented. Mild corrosion in the reactor system has continued, but the mechanism of corrosion is well understood now. Although the consequences of a corrosive failure are high, the procedures to prevent, detect, and repair corrosion damage in the reactor are well developed so that the probability of a significant occurrence and residual risk are reduced to an acceptable level. During the last inspection, relatively little damage had occurred, and repair requirements were minimal. Optimum materials of construction were determined from the intermediate scale, and these were specified for the full scale plant design.

The present unit in its "stretched" configuration has sufficient capacity for the present requirements at the plant. The reactor is continuously improved through experimentation and optimization. The system is now yielding a high economic return for the site. Significant new technology from the intermediate scale reactor was incorporated into the design for the Barry full scale reactor system. In turn, results from the Barry system will be reviewed in the future after that system has been optimized, and appropriate new technology from that plant will be transferred to Carrollton.

3.3 Full Scale (1997-present)

As originally envisioned, the full scale plant was to be installed in Carrollton, Kentucky, and to be started up in 1999. Prior to the actual commencement of the project, however, corporate long range global planning studies determined that it would be more desirable to install the full scale plant at Dow Corning's Barry, Wales, (UK) facility, where a major silicones production expansion was then in the design phase. Additionally, on-site landfill space in Barry was limited and virtually full, and there was a strong desire by company management to minimize waste for the new expanded facility. As the largest and newest silicones plant in Europe, it was projected that the superior DPR conversion technology would yield the best economic and waste reduction benefits at the Barry facility.

3.3.1 Full Scale Preliminary Engineering

Preliminary design of the full scale reactor began in January, 1997, with initial process safety studies of the reactor system. Factored cost estimates and simple block flow diagrams were completed in March. In April, 1997, additional engineers from the process engineering department

were assigned to create mass and energy balances and to study various process design alternatives. In July, the project was transferred to the Corporate Facilities Engineering Department in Midland, Michigan, to develop a Front End Package (FEP) for the engineering and construction contractor in Great Britain. At the same time, the Carrollton lead engineer relocated to the UK to preserve the continuity of project 'corporate knowledge' as the project design leader in Wales.

Detailed process flow diagrams (PFDs) and piping and instrumentation diagrams (P&IDs) were completed by Facilities Engineering in October of 1997. A Quantitative Risk Assessment (QRA) was completed. This detailed safety study showed that offsite hazards related to the reactor process were minimal. In November, the reactor purchase specification was written. In December, inquiry packages were issued for the purchase of the reactor vessel. In January of 1998, the HAZOP study was conducted. In February, advances in the technical understanding of the Carrollton intermediate scale reactor operations allowed the scope of the full scale Barry plant to be reduced. This resulted in a projected capital cost savings of \$4 million. The reactor vendor was selected, and important changes to the reactor materials of construction were agreed upon with the fabricator. In March, the engineering group in Michigan began assembling the FEP. The draft FEP was issued in April, and a final package was issued in August of 1998. With this handover, all design efforts in the USA were complete, and all future design was completed in Wales.

3.3.2 Full Scale Detailed Engineering

In July and August of 1998, design changes were recommended to reduce the capital cost of the process. Implementation of these changes began in September. Additional scope changes were recommended in October and November based on further operation of the intermediate scale reactor in Carrollton, and in December, design changes resulting from advancements in the Carrollton process finally outpaced design progress in Barry. Project cash flow was also constrained. For these two reasons, the entire capital project in Barry was suspended to await further results from the Carrollton reactor.

Barry design resumed in April of 1999. Due to the rate of design change initiations, it was decided to complete the detailed design internally, rather than to use an external engineering firm. Internal design was deemed to be more flexible and less expensive, albeit generally slower. Contract chemical engineers, mechanical engineers, and piping designers were hired to staff the project. Electrical designers and instrumentation engineers followed. By mid-1999, approximately thirty full time designers were working on the project. Further design changes from Carrollton were incorporated in July, August, and September. In September, the P&IDs were finalized for the reactor area, and the process design scope was essentially frozen. Piping layouts began in August, and by October, a three-dimensional layout review was held.

Due to the long fabrication time required, the reactor vessel was ordered in March of 1998. Other critical components directly attached to the reactor were also ordered so that their design and fabrication could occur simultaneously. Procurement of the rest of the process equipment began in October of 1999. The high pressure pump specifications were sent out for inquiry. Quotations were received from bidders for the hydrogen supply.

Also in October, the building permit application was reviewed. No significant concerns were raised during the review, and in November, formal planning permission (equivalent to a building permit) was received from the local authority.

In November and December of 1999, the filter system was redesigned. To reduce costs, an existing system was upgraded rather than constructing a new system. P&IDs were completed, and the HAZOP was completed in December.

In January of 2000, the project estimator and the discipline lead engineers completed the project cost estimate. Based on the revised scope, a capital authorization request was submitted to Dow Corning corporate management for the final project funding. The final estimate was \$2 million less than the scope that was reviewed in August of 1998. In February, orders were placed for all the remaining reactor area equipment. Orders were issued for the heat exchangers and hot oil pumps, and valve deliveries from two suppliers were reviewed. These deliveries were determined to be critical to the project schedule. DPR slurry pumps were also purchased, as delivery of these pumps was also determined to be critical to the project schedule.

Final design reviews of the reactor plant model were completed with project and manufacturing personnel in April, 2000. In May, reactor fabrication was completed at the vendor's factory, including final welds and painting. A fit test was conducted at the fabrication facility, and the reactor was shipped to Barry. The vessel was installed in the tower during the last week in the month.

In June, the design approached completion, and various engineers were redeployed to other projects. Hand-over of the project to part-time startup engineers began. Most of the design packages were issued to construction subcontractors. A low level of piping and instrumentation/electrical design continued as the final project details were being resolved. A project archive was established, and engineering documents were transferred for future reference by the startup team.

3.3.3 Full Scale Construction

Construction began in October of 1999, when the pile caps were dug and poured. Ground beam installation began the following month, and by January of 2000, the reactor building ground slab and floor were finished. The storm sewers were finished in February, and access roads were built. In March, steel erection began. The reactor vessel was installed in the tower during the last week in May, and the following month, the reactor tower steelwork was completed.

Off-site subcontract procurement and fabrication of pipe work began in June of 2000, and equipment and instrumentation began arriving onsite. By August, all major equipment was delivered, and piping of the heating system and reactor feed system began. In September, all major equipment was installed in the reactor tower. Mechanical and piping installation in the reactor tower was essentially complete by the end of the year.

The filter upgrade construction proceeded into the autumn of 2000, and was complete by the first week in December. The small volume hydrogen supply was installed in February of 2001.

3.3.4 Full Scale Commissioning

In July of 2000, two startup engineers began full time work on the commissioning effort. The startup team leader and a fourth engineer began part-time work assignments at the end of July, and the full startup team was in place by October. In December, standard operating procedures and operator training presentations were completed. Commissioning of the reactor heat transfer system began early in 2001.

Commissioning of the DPR filter system began in February of 2001. Several technical problems were experienced from March through April. A temporary solution was achieved in May, and feed to the reactor commenced on May 15, 2001.

During commissioning, a few minor equipment and operational problems were experienced. Two high pressure relief valves failed and were replaced with valves of a different design. Several hot oil system flanges were re-machined to achieve leak-proof service. Surging of a DPR pump was corrected with modifications to the operating procedures. One heat exchanger did not achieve its design temperature, but reactor operation appeared satisfactory despite this deficiency.

3.3.5 Full Scale Operation and Optimization

Operating time as of September 30, 2001, is limited. The reactor consumed 47 metric tons of waste DPR in May, and 60 metric tons in June. Complete product flow rate and composition data was not available for these campaigns. In July, on-line instrumentation was commissioned and

calibrated to measure the product flows and compositions. DPR conversion during the campaign July was calculated to be 93%. Unfortunately, due to site operational constraints unrelated to the new DPR recovery process, the campaign was curtailed. The process was not operated in August or September.

The filter operation was proven to be adequate. In July, a short campaign was completed to demonstrate filtration above design limits.

3.3.6 Full Scale Final Results

The final results of the full scale plant were as follows:

- DPR was converted at greater than 90% efficiency for brief campaigns.
- High value product was recovered.
- Full scale commercial operation was demonstrated.
- Polymerization and corrosion were not observed, but as of September 30, 2001, operating time was not yet sufficient to judge this conclusively.

4.0 ENERGY AND WASTE BENEFITS

4.1 Basis of Analysis

Silicones manufacturing technology is closely held by competitors in the industry,²⁸ and information concerning production capacities, process efficiencies, product distributions, and similar parameters is not generally divulged by silicones manufacturers. In keeping with this practice, estimated benefits in this report are based on the following information and methodology:

- Previously published data from open literature marketing reports, patents, and texts are used wherever possible.
- The conversion efficiencies from DPR hydrogenolysis technology are taken from patent literature or disclosures within this report.
- Alternative technologies such as quenching are evaluated from information in patent literature.
- Direct process selectivity to dimethyldichlorosilane and DPR are based on reported values disclosed in literature.
- Capacities for the global estimates are based on marketing reports.

Waste and energy benefits are then calculated for the total global industry, using published values and author's estimates as various inputs to the algorithms described herein. Specific details and assumptions are listed in the Appendix to this report. While this method provides reasonable results for the values utilized while concurrently protecting Dow Corning interests, it also allows the application of other values (that may be closely held by others) to assess potential benefits from adoption of the DPR recovery technology at a specific facility.

4.2 Magnitude of the DPR Waste Problem

Marketing agencies periodically assess the size of the silicones market. In 1998, production was estimated at 855,000 metric tons of silicone hydrolyzate.²⁹ All of this product is made from dimethyldichlorosilane from the direct process. In 2001, the present global production of dimethyldichlorosilane is estimated to be approximately 3.9 billion pounds per year. SRI International estimated the annual growth rate at 6% per year from 1995 through 1998.³⁰ Assuming a constant 6% growth through the next decade, and a dimethyldichlorosilane/hydrolyzate reaction ratio as noted in Appendix assumption set #8, the projected dimethyldichlorosilane production will be approximately 6.6 billion pounds per year in 2010.

²⁸ Smart, p. 7.

²⁹ Smart, pp. 7-15.

³⁰ Smart, p. 5.

For each pound of dimethyldichlorosilane produced, a fraction of the crude product is DPR. Published DPR production rates range from 3% to 8%,³¹ but the exact performance figures for each facility are not published, and individual plant efficiencies are expected to vary among the different producers. The fractions of dimethyldichlorosilane and other monomers in the product distribution also vary according to each manufacturer and the technology being practiced at each site.³² Assuming a global DPR rate of 4.5%,³³ of the crude methylchlorosilane product, the entire industry presently produces approximately 210 million pounds of DPR per year. By 2010, this will increase to about 355 million pounds (about 178 thousand US tons) per year of DPR waste.

The amount of silicon discarded by the entire industry may be derived from the DPR. In the interest of simplification, DPR is considered to consist entirely of $\text{Cl}_3\text{Si}_2\text{Me}_3$. A simple molecular weight calculation then results in a silicon fraction of about 27 wt.%. This waste will amount to approximately 96 million pounds per year of lost silicon metal in 2010, assuming the continuation of current disposal practices.

4.3 Current vs. Proposed Technology

Various DPR treatment and disposal alternatives currently exist. The alternative employed at a particular manufacturing site varies according to the technology practiced by that manufacturer. DPR can be quenched with water and alkali to yield a solid waste siloxane gel product suitable for solid landfill disposal. DPR can also be incinerated to form a solid waste silica product. This process is difficult due to the formation of glassy solids and the potential to form highly toxic dioxins. Incineration likewise creates a solid landfill material.

Certain processes already exist for partial recovery of DPR. For example, the DPR disilane fraction can be distilled and then "cracked" with chlorine, hydrogen chloride, or hydrogen. This has several disadvantages, however. First, the disilanes constitute only about 60% of the DPR, so 40% of the DPR is not recovered and must be quenched or incinerated. Second, the product formed from cracking has very low economic value. Previously published chemical literature and patents show that cracking disilanes produces a high volume of MeSiCl_3 .³⁴ Methyltrichlorosilane has low economic value and is already in a state of excess supply. Some of the excess MeSiCl_3 can be used as a feedstock for low value silica, but oversupply in the past has sometimes created the need to quench or incinerate MeSiCl_3 just like DPR. This effectively converts waste DPR to waste MeSiCl_3 . Converting one waste material to a different waste intermediate is clearly not an economically viable solution. Third, there are significant capital and processing costs of

³¹ Ullmann's, p. 25.

³² Smart, p. 7.

³³ Ward. See also further explanation in Appendix, assumption set 1.

³⁴ Freeburne, *Silicon for the Chemical Industry III*, p. 303.

disilane separation and cracking. These factors of low recovery, low economic value, and high processing costs make disilane cracking far less desirable than DPR hydrogenolysis, as discussed in this report.

Conversely, the DPR hydrogenolysis process has shown feasibility to recover 85% of the DPR as useful chlorosilanes, and is preferred to the alternatives discussed above due to its high rate of product recovery, high economic payback, and significant reduction in waste generation. DPR hydrogenolysis also offers other advantages. For example, with the improvements discovered in 1996, the co-feed monomer can be varied among MeSiCl_3 , MeHSiCl_2 and Me_2SiCl_2 to convert DPR and balance the overall monomer ratio from a basic silicones plant. This one-step process was patented by Dow Corning during the course of this project.

4.4 Market Penetration

DPR hydrogenolysis capability has been installed at both of Dow Corning's major basic plants. The technology is being optimized to consume as much DPR as possible and to minimize waste and maximize economic value. SRI International has estimated Dow Corning's 1998 market share to be 66% of the US production capacity for dimethyl silicone hydrolyzate and 42% of the total global supply.³⁵ With the technology and equipment capacity presently in place, and with future anticipated expansions, it is expected that DPR hydrogenolysis technology implementation will account for Dow Corning's full share of the US and global silicones market in the near future.

While Dow Corning is willing to license this technology to other dimethyl silicone manufacturers, investments in existing high capital cracking and chlorosilane incineration processes make it likely that alternative technologies will continue to be utilized to some degree for several years in the future. With due consideration of these factors, it is estimated that, by 2010, DPR hydrogenolysis technology will be used by 78% of the silicones production market. This level of market penetration is assumed in energy and waste savings calculated below.

4.5 Energy and Waste Savings

As discussed in Section 4.3, various methods of DPR disposal are available to the global silicones manufacturing community, depending upon the prevailing local environmental regulations and economic factors. However, for the purpose of simplifying the energy and waste calculations in this report, alkali quenching with lime slurry is assumed. This chemistry is believed to be the main US alternative employed for DPR disposal.

As discussed in Section 4.2, it is anticipated that there will be a need to dispose of approximately 355 million pounds of DPR containing approximately 96 million pounds silicon in the year 2010. Applying a

³⁵ Smart, p. 7-15.

process recovery factor of 85% and a market penetration of 78% yields a net potential recovery of slightly over 66% of what would otherwise be discarded. Thus, in the year 2010, the total DPR recovered from this new technology is estimated to be approximately 235 million pounds, which contains approximately 64 million pounds of silicon. Of interest is what this material represents in terms of potential energy savings and avoided environmental discharge.

4.5.1 Energy Savings

Silicon production is a very energy intensive process. Electricity usage alone is approximately 6.6 kWh per pound of silicon. Coal, wood chips, and coke add carbon to the quartz to reduce the oxygen to carbon monoxide, silicon monoxide, and silicon carbide. Additional energy is required to manufacture the electrodes, which are consumed during the silicon smelting process. A table of energy usage distribution is shown below³⁶:

Table 3: Energy Usage for the Manufacture of Silicon*

	Usage per pound silicon	BTU per unit	Total Energy BTU/lb silicon
Quartz	2.747 lb/lb	65 BTU/lb	179 BTU/lb
Coke	0.24 lb/lb	15,800 BTU/lb	3,792 BTU/lb
Coal	1.057 lb/lb	13,000 BTU/lb	13,741 BTU/lb
Dry wood	1.533 lb/lb	8,500 BTU/lb	13,031 BTU/lb
Electrode	0.116 lb/lb	80,000 BTU/lb	9,280 BTU/lb
Electricity	6.6 kWh/lb	10,500** BTU/kWh	69,300 BTU/lb
Total energy per pound silicon			109,322 BTU/lb

* Typical for a 3f AC, 20MW, submerged arc, open smelting furnace
 ** Heat rate assumes electrical generation plant efficiency of 32.5%

³⁶ Adapted from Alanko and Whiteley, Attachment 4. (For consistency, the same energy basis is used here as in the referenced 1993 document. Similar energy values can be found in the Schei text.)

On the other hand, the DPR hydrogenolysis process for recovering DPR uses relatively little energy, requiring only 2,721 BTU/lb of silicon recovered. The high waste conversion rate and low energy usage yield high energy savings for this technology. Potential energy savings are calculated in Table 4 below.

Table 4: Energy Savings

A	B	C	D = B - C	E	F = D x E
Description	Current Technology (BTU/lb Si)	Proposed Technology (BTU/lb Si)	Net energy savings (BTU/lb Si)	Pounds of Si Saved per year in 2010	Energy savings in Year 2010 (10 ¹² BTU/yr)
Quartz	179		179	63,773,532	0.011
Coke	3,792		3,792	63,773,532	0.242
Coal	13,741		13,741	63,773,532	0.876
Electricity	69,300	2,721	66,579	63,773,532	4.246
Dry wood chip	13,031		13,031	63,773,532	0.831
Electrode	9,280		9,280	63,773,532	0.592
Total	109,322	2,721	106,602	63,773,532	6.798

Although the case here is based on quenching DPR, comparison to incineration might yield more favorable energy savings, since high temperature combustion sometimes requires additional fuel and because heat recovery of incinerated silanes is technically difficult due to silica fouling. In any case, the potential yearly energy savings of 6.8×10^{12} BTU due to silicon recovery alone is considerable by any measure.

4.5.2 Waste Reduction

The DPR is quenched with lime and landfilled as solid siloxane waste. Calcium chloride salt is produced and must be landfilled or flushed out with wastewater. As before, application of a process recovery factor of 85% and a market penetration of 78% (and appropriate units conversions) yields a net potential recovery of slightly over 66%, leaving the remaining 33% subject to traditional disposal methods. Waste reduction is shown in Table 5 on the following page:

Table 5: Waste Reduction

A	B	C	D = B - C	E	F = D X E
Description	Current Technology. Tons waste per ton DPR produced. (100% of DPR production processed as waste.)	Proposed Technology at 85% conversion and 78% market penetration. Tons waste per ton DPR produced. (33.7% of DPR production processed as waste.)	Waste Reduction per Unit. Current less proposed. Tons waste avoided per ton DPR produced.	Global DPR Production in 2010. Tons DPR.	Total Waste Reduction in year 2010. Tons waste avoided.
Quenched DPR to landfill	1.52	0.51	1.01	177,765	179,145
CaCl ₂ to land or water	0.80	0.27	0.53	177,765	94,522
Waste water	6.87	2.32	4.55	177,765	809,687
Total	9.19	3.10	6.09	177,765	1,083,355

5.0 **BUSINESS CONSIDERATIONS**

5.1 **Economic Attractiveness**

Metallurgical grade silicon contributes the greatest share toward the variable cost of basic chlorosilane intermediates with the high energy cost associated with silicon production being the major manufacturing cost. Another significant contributor to variable cost is the loss of chloride due to process inefficiencies, e.g., chloride loss as salt in the lime quenching of DPR. The cost to landfill the solids from the quenching is also considerable. Reduction or avoidance of these costs provides significant economic incentive for implementation of DPR hydrogenolysis technology.

5.1.1 **Net Present Value Analysis**

To demonstrate the economic benefit of this technology, a net present value (NPV) analysis was performed. Since the cost structures and process efficiencies of the silicones producers are closely held industrial secrets,³⁷ published costs and efficiencies were used to perform this analysis. *These published efficiencies, costs and the attached NPV analyses deliberately do not reflect the cost structure at Dow Corning.* However, they do provide a basis for comparison of the waste disposal alternatives, and they do clearly demonstrate the favorable economic incentives for any silicones producer to convert DPR to valuable monomers by means of this technology.

The analysis was performed as follows. Spot market silicon and bulk sales methyl chloride prices were obtained from published external sources.^{38,39,40} A published crude chlorosilane product distribution was assumed as shown on page 4⁴¹ and Appendix assumption set #1. Capital costs were assumed based on the cost plan for this project. Typical plant economic factors and economic analysis methods were employed according to the classic chemical engineering text by Max Peters and Klaus Timmerhaus.⁴²

For the basic analysis of a single "theoretical" large scale hydrolyzate plant, a 100,000 metric ton per year silicones plant size was chosen. The operating efficiencies and economics for three DPR disposal alternatives were compared: 1) hydrogenolysis, 2) quenching, and 3) off-site

³⁷ Smart, p. 7.

³⁸ Chemical Market Reporter.

³⁹ CRU Monitor.

⁴⁰ "US Geological Survey", p. 69.3.

⁴¹ Ullmann's, p. 25.

⁴² Peters and Timmerhaus, pp. 312-315.

incineration (i.e., toll incineration). The basis is an existing operating facility with an existing on-site quencher or existing off-site toll incineration facility. The economics would improve further if the capital costs of these other waste disposal alternatives were added for a green field site analysis. A 15% internal rate of return (IRR) was assumed. For full details, see the relevant assumptions and calculations provided in the Appendix. Summary results are shown in the table below.

Table 6: Economic Comparison of DPR Disposal Alternatives

Technology Alternative	Capital cost [millions]	Cash flow (Year 1) [millions]	Ten Year Net Present Value [millions]	Relative NPV [millions]
DPR Hydrogenolysis	\$12.13	\$3.08	\$0.90	\$0.00
DPR Quenching (existing)	\$0.00	(\$0.95)	(\$3.91)	(\$4.81)
DPR Incineration (off-site)	\$0.00	(\$4.46)	(\$18.42)	(\$19.32)

Hydrogenolysis requires a high initial capital investment, but provides a positive cash flow and positive net present value. The relative net present value is also shown above as the difference between hydrogenolysis and the other alternatives.

A sensitivity analysis was also performed to show the effect of certain economic variables. Figure 4, on the following page, shows the effect of economy of scale. For very small plants, the high capital cost outweighs the payback in raw material savings. The same effect is true for the rate of DPR production. As the rate of DPR production is varied from 1% to 10%, very low DPR rates create negative net present value. Higher rates create very favorable NPV. The decision point (at 15% IRR) is between 2% (relative NPV) and 4% (absolute NPV) DPR production rate. DPR generation above this threshold makes the investment attractive from a financial viewpoint.

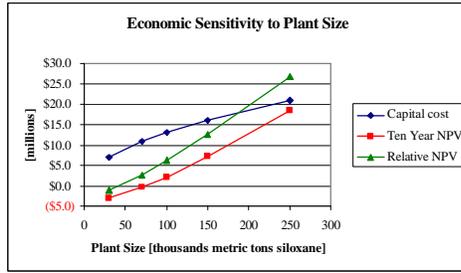


Figure 4: Economic Sensitivity to Plant Size

The price of dimethyldichlorosilane also affects the economic analysis. At very low silicon and methyl chloride prices, the economic incentive to recover waste is eroded. The decision point for a 100,000 metric ton siloxane plant (15% IRR) at 4.5% DPR rate is approximately 25 cents per pound. At Me_2SiCl_2 costs significantly below this amount, it is more economically favorable to quench DPR and landfill the waste.

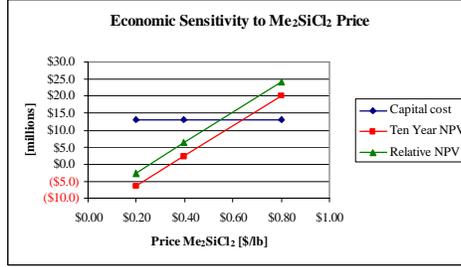


Figure 5: Economic Sensitivity to Me_2SiCl_2 Price

5.1.2 Other Business Considerations

Compared to disilane cracking technology, DPR hydrogenolysis offers higher conversion (85% versus about 60%) and more favorable product monomer distributions.⁴³ By using alternative monomer co-feeds (as described in US Patent 5,606,090), it is possible to adjust the output of the direct process to match product demand. By varying the co-feed monomer, the net monomer distribution from the DPR conversion process can be varied in the ranges of 0% to 39% MeSiCl₃, 1% to 64% Me₂SiCl₂, and 0% to 49% MeHSiCl₂.⁴⁴ Up to 16% Me₂HSiCl can be made when this monomer is in high demand. The high conversion and flexibility provide significant advantages over potentially competing technical alternatives.

5.2 Policy/Regulatory

Future chlorine emissions, even in the form of inorganic salts, are likely to be regulated more stringently than is the current practice. Incineration is especially a concern due to the possibility to form dioxins from the combustion of organic chlorides. Solid waste landfill is also likely to become more heavily regulated in the future.

Waste reduction and recycling are prime objectives of the American Chemistry Council. Voluntary programs, such as the Responsible Care[®] initiative, emphasize the need to make significant and sustained reductions in waste volumes. Dow Corning is participating in this initiative, which promotes a goal of a 40% reduction of wastes emitted to the environment by the end of 2004, using 1997 as the base year. Many manufacturers are adopting "zero discharge" targets to benchmark new technologies and to assess existing manufacturing processes. Increasing public pressure is being applied on manufacturers to reduce their chemical process waste. Even assuming marginal economic benefits, there are strong regulatory and public relations incentives for chemical manufacturers to adopt "green technology".

5.3 Industrial Competitiveness

All domestic and international silicone producers have the same problems associated with the DPR. Each producer's environmental costs will continue to escalate, with further need for landfill space and the potential for escalating environmental regulation. Without the novel waste conversion technology developed by this project, silicone producers will be at a significant cost disadvantage in manufacturing methyl silicones.

5.4 Commercialization plans

Dow Corning has installed full capability to utilize this technology at the Barry, Wales, facility, and is expanding its intermediate scale facility at the Carrollton, Kentucky, site to maximize its waste recycling

⁴³ Freeburne, *Silicon for the Chemical Industry III*, p. 307.

capacity at those plants. Thus, with Dow Corning's current and anticipated implementation alone, the technology may soon process DPR for 66% of US silicones market and 42% of the global market.⁴⁵ It is hoped that this technology will be adopted by others in the industry under licensing agreements with Dow Corning.

5.5 Foreign Trade

Almost forty percent of all silicones are manufactured in the United States.⁴⁶ Implementation of this technology by U.S. manufacturers will lower hydrolyzate manufacturing costs compared to foreign producers. The foreign producers will continue to bear the continued costs of chloride ion loss and silicon inefficiency. The lower cost position of U.S. manufacturers may allow them to increase their share of the global silicone market.

⁴⁴ Brinson et al., US Patent 5,606,090.

⁴⁵ Smart, p. 7-15.

⁴⁶ *Ibid.*

6.0 SUMMARY

Dow Corning has demonstrated the commercial viability of the new DPR hydrogenolysis technology developed by this project. The intermediate scale reactor started up in Carrollton, Kentucky, in 1997 and continues to operate at efficiencies above 85% DPR conversion. The reactor in Barry, Wales, started up in 2001. Its operating history is currently limited, but initial performance results are favorable, as is the long-term operational and economic prognosis.

Significant problems were experienced at the pilot scale and early intermediate scale with product recovery, polymerization within the reactor, corrosion, and equipment reliability. Product recovery problems were solved at the later intermediate scale. Problems with corrosion and polymerization have been greatly improved, but still present concerns that require diligence to preclude adverse effects.

DPR hydrogenolysis technology significantly reduces waste generation and energy usage compared with conventional silicones manufacturing technology. It offers a significant economic savings compared with conventional waste quenching technology for a large scale siloxanes manufacturing plant.

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APPENDIX 1

Economic and Waste Reduction
Analyses and Assumptions

DPR Hydrogenolysis

Amounts in thousands US Dollars

Economic analysis as per Peters & Timmerhaus, Plant Design and Economics for Chemical Engineers, 1979, p. 314.

Year	0	1	2	3	4	5	6	7	8
Fixed capital investment	\$12,135								
Working capital	\$121								
Total capital investment	\$12,256								
Annual income (sales)		\$7,001	\$7,141	\$7,284	\$7,429	\$7,578	\$7,729	\$7,884	\$8,039
Annual manufacturing costs									
Raw materials									
DPR		\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$0
Monomers		\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$0
Hydrogen		\$579	\$590	\$602	\$614	\$626	\$639	\$652	\$665
Lime		\$46	\$47	\$48	\$49	\$50	\$51	\$52	\$53
Labor		\$169	\$172	\$176	\$179	\$183	\$186	\$190	\$193
Utilities		\$200	\$204	\$208	\$212	\$216	\$221	\$225	\$229
Maintenance and repairs		\$849	\$866	\$884	\$901	\$919	\$938	\$957	\$976
Operating supplies		\$127	\$130	\$133	\$135	\$138	\$141	\$143	\$146
Laboratory charges		\$8	\$9	\$9	\$9	\$9	\$9	\$10	\$10
Patents and royalties		\$140	\$143	\$146	\$149	\$152	\$155	\$158	\$161
Local taxes and insurance		\$243	\$248	\$252	\$258	\$263	\$268	\$273	\$278
Plant overhead		\$509	\$519	\$530	\$540	\$551	\$562	\$573	\$584
Landfill costs		\$141	\$144	\$147	\$150	\$153	\$156	\$159	\$162
Incineration costs		\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$0
Total annual mfg costs		\$3,012	\$3,072	\$3,134	\$3,196	\$3,260	\$3,325	\$3,392	\$3,459
Annual general expenses									
Administrative		\$34	\$34	\$35	\$36	\$37	\$37	\$38	\$39
Distribution and selling		\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$0
Research and development		\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$0
Total annual general expenses		\$34	\$34	\$35	\$36	\$37	\$37	\$38	\$39
Total product costs		\$3,046	\$3,107	\$3,169	\$3,232	\$3,297	\$3,363	\$3,430	\$3,499
Annual operating income		\$3,955	\$4,034	\$4,115	\$4,197	\$4,281	\$4,367	\$4,454	\$4,543
Annual depreciation		\$2,043	\$1,857	\$1,671	\$1,486	\$1,300	\$1,114	\$928	\$743
Income before tax		\$1,912	\$2,177	\$2,444	\$2,712	\$2,981	\$3,253	\$3,526	\$3,800
Income after tax		\$1,033	\$1,176	\$1,320	\$1,464	\$1,610	\$1,756	\$1,904	\$2,053
Annual cash income		\$3,075	\$3,033	\$2,991	\$2,950	\$2,910	\$2,871	\$2,832	\$2,793
Annual cash flow	(\$12,256)	\$3,075	\$3,033	\$2,991	\$2,950	\$2,910	\$2,871	\$2,832	\$2,793
Ten year net present value	\$896								

DPR Quenching

Amounts in thousands US Dollars

Economic analysis as per Peters & Timmerhaus, Plant Design and Economics for Chemical Engineers, 1979, p. 314.

Year	0	1	2	3	4	5	6	7
Fixed capital investment	\$0							
Working capital	\$0							
Total capital investment	\$0							
Annual income (sales)		\$0	\$0	\$0	\$0	\$0	\$0	\$0
Annual manufacturing costs								
Raw materials								
DPR		\$0	\$0	\$0	\$0	\$0	\$0	\$0
Monomers		\$0	\$0	\$0	\$0	\$0	\$0	\$0
Hydrogen		\$0	\$0	\$0	\$0	\$0	\$0	\$0
Lime		\$308	\$314	\$320	\$327	\$333	\$340	\$347
Labor		\$169	\$172	\$176	\$179	\$183	\$186	\$190
Utilities		\$75	\$77	\$78	\$80	\$81	\$83	\$84
Maintenance and repairs		\$70	\$71	\$73	\$74	\$76	\$77	\$79
Operating supplies		\$11	\$11	\$11	\$11	\$11	\$12	\$12
Laboratory charges		\$8	\$9	\$9	\$9	\$9	\$9	\$10
Patents and royalties		\$0	\$0	\$0	\$0	\$0	\$0	\$0
Local taxes and insurance		\$20	\$20	\$21	\$21	\$22	\$22	\$23
Plant overhead		\$119	\$122	\$124	\$127	\$129	\$132	\$134
Landfill costs		\$942	\$961	\$980	\$1,000	\$1,020	\$1,040	\$1,061
Incineration costs		\$0	\$0	\$0	\$0	\$0	\$0	\$0
Total annual mfg costs		\$1,722	\$1,757	\$1,792	\$1,828	\$1,864	\$1,902	\$1,940
Annual general expenses								
Administrative		\$34	\$34	\$35	\$36	\$37	\$37	\$38
Distribution and selling		\$0	\$0	\$0	\$0	\$0	\$0	\$0
Research and development		\$0	\$0	\$0	\$0	\$0	\$0	\$0
Total annual general expenses		\$34	\$34	\$35	\$36	\$37	\$37	\$38
Total product costs		\$1,756	\$1,791	\$1,827	\$1,864	\$1,901	\$1,939	\$1,978
Annual operating income		(\$1,756)	(\$1,791)	(\$1,827)	(\$1,864)	(\$1,901)	(\$1,939)	(\$1,978)
Annual depreciation		\$0	\$0	\$0	\$0	\$0	\$0	\$0
Income before tax		(\$1,756)	(\$1,791)	(\$1,827)	(\$1,864)	(\$1,901)	(\$1,939)	(\$1,978)
Income after tax		(\$948)	(\$967)	(\$987)	(\$1,006)	(\$1,026)	(\$1,047)	(\$1,068)
Annual cash income		(\$948)	(\$967)	(\$987)	(\$1,006)	(\$1,026)	(\$1,047)	(\$1,068)
Annual cash flow		\$0	(\$948)	(\$967)	(\$987)	(\$1,006)	(\$1,047)	(\$1,068)
Net present value		(\$3,913)						

DPR Incineration (off-site)

Amounts in thousands US Dollars

Economic analysis as per Peters & Timmerhaus, Plant Design and Economics for Chemical Engineers, 1979, p. 314.

Year	0	1	2	3	4	5	6	7
Fixed capital investment	\$0							
Working capital	\$0							
Total capital investment	\$0							
Annual income (sales)		\$0	\$0	\$0	\$0	\$0	\$0	\$0
Annual manufacturing costs								
Raw materials								
DPR	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$
Monomers	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$
Hydrogen	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$
Lime	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$
Labor	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$
Utilities	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$
Maintenance and repairs	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$
Operating supplies	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$
Laboratory charges	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$
Patents and royalties	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$
Local taxes and insurance	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$
Plant overhead	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$
Landfill costs	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$
Incineration costs	\$8,265	\$8,430	\$8,599	\$8,771	\$8,946	\$9,125	\$9,308	\$
Total annual mfg costs		\$8,265	\$8,430	\$8,599	\$8,771	\$8,946	\$9,125	\$9,308
Annual general expenses								
Administrative	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$
Distribution and selling	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$
Research and development	\$0	\$0	\$0	\$0	\$0	\$0	\$0	\$
Total annual general expenses		\$0	\$0	\$0	\$0	\$0	\$0	\$0
Total product costs		\$8,265	\$8,430	\$8,599	\$8,771	\$8,946	\$9,125	\$9,308
Annual operating income		(\$8,265)	(\$8,430)	(\$8,599)	(\$8,771)	(\$8,946)	(\$9,125)	(\$9,308)
Annual depreciation		\$0	\$0	\$0	\$0	\$0	\$0	\$0
Income before tax		(\$8,265)	(\$8,430)	(\$8,599)	(\$8,771)	(\$8,946)	(\$9,125)	(\$9,308)
Income after tax		(\$4,463)	(\$4,552)	(\$4,643)	(\$4,736)	(\$4,831)	(\$4,928)	(\$5,026)
Annual cash income		(\$4,463)	(\$4,552)	(\$4,643)	(\$4,736)	(\$4,831)	(\$4,928)	(\$5,026)
Annual cash flow	\$0	(\$4,463)	(\$4,552)	(\$4,643)	(\$4,736)	(\$4,831)	(\$4,928)	(\$5,026)
Net present value	(\$18,419)							

Assumptions and Calculations for Waste Savings and Economic Analysis

1. Crude chlorosilane composition according to following distribution

Specie	Range [weight percent]	Typical value [weight percent]
Me ₂ SiCl ₂	70% - 90%	83.4%
MeSiCl ₃	5% - 15%	7.1%
Me ₃ SiCl	2% - 4%	2.5%
MeHSiCl ₂	1% - 4%	2.2%
Me ₂ HSiCl	0.1 - 0.5%	0.3%
DPR	3% - 8%	4.5%

Sources: Range from Ullmann's Encyclopedia, Vol. A-24, p. 25.

Typical value for minor species set from Ullmann's at approximately middle of range with minors total = 5%.

Typical value for main species set from US Patent 4,500,724; Example 3; column 11; Table VI; lines 19-31.

minors = 5% (estimate by author of this report)

T/D = 0.085 (middle of range of data reported; "T/D" is the

ratio of MeSiCl₃:Me₂SiCl₂)

DPR = 4.5% (middle of range of data reported)

Note: These two references are used to set the global DPR rates. They are selected as general references from the industry. US 4,500,724 is an expired patent now in the public domain. This is a 96 hour continuous operation example claimed by the inventors to show "satisfactory dimethylchlorosilane production rate while maintaining a high degree of selectivity...."

2. DPR composition according to following distribution

Specie	Range [weight percent]	Typical value [weight percent]
Disilanes	30% - 80%	60%
Silmethylenes	5% - 30%	20%
High Boilers	10% - 40%	20%

Source: US Patent 5,430,168.

3. DPR conversion with hydrogenolysis technology 85%
Market penetration in 2010: 78%

4. Raw material and product costs

MeCl	\$0.34	Chemical Market Reporter, 03Dec01, industrial bulk, tanks, f.o.b. works, per pound
Si	\$0.609	per pound (see footnotes 38, 39, and 40 on page 27 and references in bibliography)
lime	\$70	per ton dry CaO
lime	\$0.035	per pound dry CaO

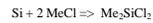
5. Environmental disposal costs

landfill	\$60	per ton
incineration	\$0.40	per pound

6. Overall chemical reaction for silicon metal

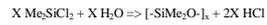


7. Chemical reactions for chlorosilane manufacture



Specie	MW	moles	Ratio	
			lb/lb	Cost/lb
Si	28.1	1	0.22	\$0.13
MeCl	50.45	2	0.78	\$0.27
Me ₂ SiCl ₂	129.0	1		\$0.40

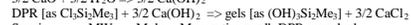
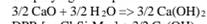
8. Chemical reactions for silicone manufacture



Specie	MW
Me ₂ SiCl ₂	129.0
-SiMe ₂ O-	74.1
Ratio	1.741

9. Chemical reactions for DPR quenching

Simplifying assumption: all DPR is Cl₃Si₂Me₃



Specie	MW	Moles	Mass ratios per lb DPR quenched
Cl ₃ Si ₂ Me ₃	207.6	1	1.000 lb basis
CaO	56.1	1.5	0.405 lb consumed
gels	152.2	1	0.733 lb formed
CaCl ₂	111.0	1.5	0.802 lb formed
Ca(OH) ₂	74.1	1.5	0.536 lb intermediate

Excess lime	5%
CaO ratio	0.426 lb CaO fed/lb DPR quenched
Excess slaked lime in solid waste	0.027 lb excess Ca(OH) ₂ /lb DPR quenched
Total dry solid waste	0.760 lb dry solid/lb DPR quenched
Water ratio in the gel	50% by weight
Water held in the solid waste	0.760 lb/lb DPR
Total wet gel waste	1.520 lb wet gel/lb DPR
Ratio CaCl ₂	0.802 lb CaCl ₂ /lb DPR
Waste water	6.87 lb H ₂ O/lb DPR

10. Capacity of plant for economic analysis

According to CEH Marketing Report, Sept. 2000, there are eleven hydrolyzate plants operating globally with smallest at 33,000 metric tons siloxane and largest at 210,000 metric tons siloxane

Basis 100,000 metric tons siloxane basis for analysis

383 million lb/yr Me₂SiCl₂ rate

20.7 million lb/yr DPR produced in crude

17.6 million lb/yr DPR converted by hydrogenolysis

3.1 million lb/yr DPR unconverted by hydrogenolysis

17.6 million lb/yr valuable chlorosilane from DPR converted by hydrogenolysis

10.1 million lb/yr siloxane from DPR converted by hydrogenolysis (assuming MW of Me₂SiCl₂)

\$7.00 million/yr valuable chlorosilane raw material value (chlorosilane price from assumption set #7)

11. Calculation of cost of only quenching partial DPR unrecovered from hydrogenolysis

3.1	million lb/yr DPR quenched
1.3	million lb/yr lime
\$46,181	cost of lime
4.7	million lb/yr gels
\$141,351	landfill cost

12. Calculation of cost of quenching all DPR

20.7	million lb/yr DPR quenched
8.8	million lb/yr lime
\$307,877	cost of lime
31.4	million lb/yr gels
\$942,337	landfill cost

13. Calculation of cost of incinerating all DPR at off-site hazardous waste incinerator

20.7	million lb/yr DPR incinerated
\$8.3	million, incineration costs

14. Hydrogenolysis plant sizing and cost

Capital cost	\$12.1	million, based on log-log regression of capital
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15. Assumptions for economic analysis

Inflation rate	2% per year (cost basis is year one, inflation starting in year two)
Working capital	1% of capital for spare parts, estimate by author
H ₂ costs	\$0.58 million per year
Labor	0.5 worker/unit/shift; P&T, p. 195, typical labor requirement for continuous reactor
\$50,000	Approximate annual salary operator/supervisor/engineer estimate by author
0.25	Supervisor and junior engineer; many years effort to support process, estimate by author
1.5	Salaries/benefits multiplier, estimate by author
Utils - rxn. with H ₂	\$200,000 per year, estimate by author
Utils - quench	\$75,000 per year, estimate by author
Maintenance	7% of fixed capital, as complex/severe process, low side, Peters & Timmerhaus, p. 201
Operating supplies	15% of maintenance and repairs, Peters & Timmerhaus(P&T), p. 201
Laboratory	5% of operating labor, P&T, p. 201
Patents/royalties	2% of product cost, P&T, p. 201; product taken as chlorosilane value
Taxes	1% of fixed capital, as low populated area, P&T, p. 202
Insurance	1% of fixed capital, P&T, p. 202
Overhead	50% of total labor, supervision & maintenance, P&T, p. 203
Administration	20% of operating labor, P&T, p. 204
Distribution	0% savings claimed on raw material costs
R&D	0% for this increment
Interest	5% of direct fixed capital, P&T, p. 204
Depreciation	Sum of the years digits method (for simplicity)
Tax rate	46% P&T, p. 314
Interest rate	15%
Quencher cap cost	\$1,000,000 (used to calculate maintenance, insurance, etc.), estimate by author