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RECOVERY OF VALUABLE CHLOROSILANE INTERMEDIATES BY A NOVEL WASTE CONVERSION PROCESS

Technical Report for Phase IIIB (Progress)
June 98 - September 99

By

Kurt E. Anderson

March 2000

Work Performed Under Contract No. DE-FC04-94AL99566

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

By
Dow Corning Corporation
Midland, Michigan

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P.O. Box 994

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ABSTRACT

From June 1998 through September 1999, direct process residue (DPR, a waste byproduct) hydrogenolysis has been studied at a large Pilot Plant within Dow Corning's Carrollton, Kentucky, plant. The system reacts filtered DPR with chlorosilane monomers at high temperature and pressure. The process routinely demonstrates DPR conversions from 59% to 89% on a monthly basis. The reaction product contains high concentrations of valuable monomers such as dimethyldichlorosilane and methyldichlorosilane. An expansion of the current unit's capacity is planned to be on-line by the end of 2000. Furthermore, a larger DPR hydrogenolysis reactor based on these results is being designed for operation in Europe at Dow Corning's Barry, Wales, site.

PREFACE

The objective of this Dow Corning Corporation and DOE cost-shared project is to develop a novel waste conversion process for the recovery of valuable chlorosilane intermediates. 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 , KY. Phase IIIB, Engineering Development - Full Scale, is the development of the commercial system at Barry, Wales. Earlier work is described in report DOE/AL/99566-1, "Recovery of Valuable Chlorosilane Intermediates by a Novel Waste Conversion Process, Technical Report for Phase IIIA (Final) and Phase IIIB (Progress)", and is recommended reading as a full technical preface to material herein. The second year of that development is described in this report. Finally, Phase IV, Demonstration - Full Scale, which start when the development is completed, will conclude the project.

ACKNOWLEDGMENTS

Brian Volintine is the Program Manager in the DOE Office of Industrial Technologies. Nancy Hoffman is Contracting Officer for the DOE Albuquerque Operations Office. Ken Lucien is the Project Manager for the DOE Albuquerque Operations Office. Steve Freeburne is a Dow Corning Corporation Director of Science and Technology for the Industry/Business Unit, of which the Silicon Methyl Intermediates (SMI) department is a part. Charles Hall is the Core Process Engineering Manager within SMI. Ben Franklin is a Contracts Specialist in the Federal Business and Contract Development Department of Dow Corning Corporation. Darrell Whiteley and J. Ashley Brinson were past Principal Investigators; Mr. Brinson is now the Project Leader in Barry. William Brady is a Senior Process Engineer currently responsible for development and expansion of the Carrollton hydrogenolysis process. Christine Stump is the Manufacturing Engineer responsible for the daily operation of the Carrollton unit.

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1. INTRODUCTION

1.1 The DPR Problem

Dow Corning produces dimethyldichlorosilane (Me_2SiCl_2) by the reaction of methyl chloride and silicon metal in a system known as the "direct process". 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.

Direct process residue is a waste stream. Selectivity can be improved by manipulating the operating parameters of the fluidized bed reactor (FBR), but it is impossible to suppress formation of DPR.

In Barry, DPR is separated from the desirable monomers, then quenched with water and lime slurry to form solid gels. The gels are landfilled on site.

In Carrollton, DPR is separated from the monomers, then further processed. Methylchlorodisilanes (MCDS) are distilled from the silmethylenes and other higher boiling species. MCDS is shipped to the Midland thermal cracker process where the material is reacted at high temperature with hydrogen chloride to form monomers. The cracker product contains a relatively high fraction of low-value monomers. The cracker process also has a history of poor maintenance reliability, a high frequency of safety incidents and a number of failures due to corrosion. The cracker cannot process silmethylenes and higher boiling chlorosilanes. Cracker product is shipped back from Midland to Carrollton for distillation in the main process train. In Carrollton, the bottoms of the MCDS column are quenched with water and lime slurry, then landfilled as in Barry.

A process which recycles DPR internally and produces a high value product offers significant economical advantages over the existing cracker process and the various recycle programs. The benefits include environmental (reduced landfill, reduced quenching costs), raw material conservation (recovered chloride and silicon), and valuable monomer production.

1.2 Past Efforts - Literature since May 1998

In July 1998, Wood published "The Chemistry of Disilane Hydrogenolysis" [1]. In it he outlined the development of a new reaction scheme involving a novel complex intermediate which provides a better explanation of the experimental data observed both in the laboratory and the plant. Dehydrocoupling and disproportionation with polymerization also occur under the conditions of the hydrogenolysis reaction, leading to polysilanes and unwanted solids. Unfortunately, since the different reaction paths have a common intermediate, the reactions may not be conducted independent of one another. Experimental conditions can be chosen, however, to limit, though not eliminate, the unwanted reaction pathways.

In November 1998, Bolland reported on the "Post Start-up Optimization" of the Pilot Plant II DPR Hydrogenolysis unit [2]. He listed the following significant learnings:

- proper monomer co-feed can reduce hydrogen feed requirements, lower the reaction initiation temperature, and enable the reaction to occur at lower temperatures
- a minimum hydrogen-to-chlorosilane feed ratio was demonstrated at four times lower than the design feed ratio
- no reactor downtime was attributed to solids formation in the reactor
- pitting of the reactor lining was observed on the bottom head
- very high hydrogen conversion can be obtained via total liquid product take-off

In June 1999, Bolland, Coldman and Bellingham reported on a "Filter Start-up" in Barry, Wales [3]. While not part of a hydrogenolysis unit at the time, the filter's great success later led Barry engineers to consider sharing its capacity on a campaign basis with a future hydrogenolysis unit. The filter was installed at the plant as part of a program to enable closure of the site quench pond. The filter cake from the filter continues to be quenched as before. However, the filtrate is either incinerated off-site or recycled back to its originating process for recovery of usable material. Significant overall reduction in the quantity of material quenched from the process were immediately achieved. The reductions were the result of recycling the filtrate back to the originating process to recover usable material. Previously the filtrate was used to slurry the solids prior to quenching. Due to its excess capacity, the potential for using this filter as part of the new hydrogenolysis process being designed for the Barry site was evaluated via a trial.

In August 1999, Brady, Wood, and Payne reported on "Metal Alloy Coupon Testing" [4]. The Carrollton hydrogenolysis reactor had been inspected twice since it was placed in service October 1997. Both inspections, July 1998 and March 1999, revealed pitting of the reactor cladding. The pitting could have occurred during normal operations or during periodic caustic soda washing to remove chlorosilanes and solid residues. This laboratory experiment was an effort determine if pitting of the metal could occur under anhydrous normal operational conditions. Following exposure of the coupons to the hydrogenolysis chemical environment and high temperature for 408 hours, no weight loss was observed compared to initial coupon weights. All coupons were evaluated under a 30 power stereo microscope. No pitting was noted on any of the coupons. Further, the AISI type 316L stainless steel sample was examined in a Scanning Electron Microscope and compared to a virgin 316L coupon. No pitting was identified. Previous experience with coupons in the production scale reactor shows pitting can be clearly observed with less than 50x magnification. It appears possible that the current aqueous wash techniques employed may be causing the pitting. The current practice of slow addition of the caustic, not hydraulically filling the reactor, and the long time that weak acids may be in the system prior to head removal and water blasting all could contribute to the pitting. A future caustic cleaning strategy was suggested. Metal alloy coupon testing is discussed further in Section 2.3.

1.3 Process Description of Pilot Plant II

A sketch of the process is given in Figure 1. DPR from the adjoining FBR's reboiler or from the site's DPR tank is transferred to the dirty DPR tank. A DPR pump operates continuously to recycle material in a loop from the bottom of the dirty DPR tank through a service water cooler and back to the tank to keep silicon solids suspended and precipitate some aluminum chloride ($AlCl_3$) out of solution. Methylchlorodisilanes (MCDS) are transferred to the feed tanks as a substitute for DPR, and used to back-flush the DPR filter.

To remove silicon solids, DPR is pumped to the filter from the dirty DPR tank. Filtrate is routed to a mix tank. The filter is cleaned in place with nitrogen and MCDS. Solids are discharged into the site's DPR tank. After every batch of filtrate is collected, monomer is added to prepare the reactor feed mixture to be transferred to the feed tank. Chlorosilane monomer is transferred to the mix tank from a plant header originating in the tank farm.

A positive displacement feed pump pressurizes the mixed chlorosilane feed to reactor pressure. Chlorosilane feed is heated with hot oil in a finned-tube preheater. Chlorosilanes enter the reactor on the bottom or the top, depending on valve arrangements. Typically, chlorosilanes are fed to the bottom of the reactor to help prevent plugging of the bottom nozzles and piping with reaction by-products that are solid.

Hydrogen (H_2) is supplied from a liquid hydrogen tank maintained by a vendor. Hydrogen liquid from the tank is compressed beyond reactor pressure with a reciprocating pis ton pump. The high-pressure liquid hydrogen is then vaporized in an ambient air vaporizer and stored in a tube bank. From the tube bank, H_2 is regulated to supply pressure. A control valve in Pilot Plant II regulates flow at reactor pressure. Hydrogen is preheated with hot oil in a shell and tube preheater. H_2 enters the reactor at the bottom or the top, depending on valve arrangements. Typically, H_2 is fed to the bottom of the reactor.

The hot oil system uses a silicone heat transfer fluid. Oil from an expansion tank is pumped to the electric heater. A pair of automatic valves then divert flow to an emergency air fan cooler or directly to the preheaters and reactor. Typically ~10% of flow is routed through the cooler, keeping its tubes warm to avoid thermal shock during an emergency that calls for full cooling. Power input to the heater is adjusted by means of a silicon controlled rectifier (SCR). A temperature controller for the oil loop automatically controls power. To adjust reactor temperature, the setpoint to the oil loop is changed.

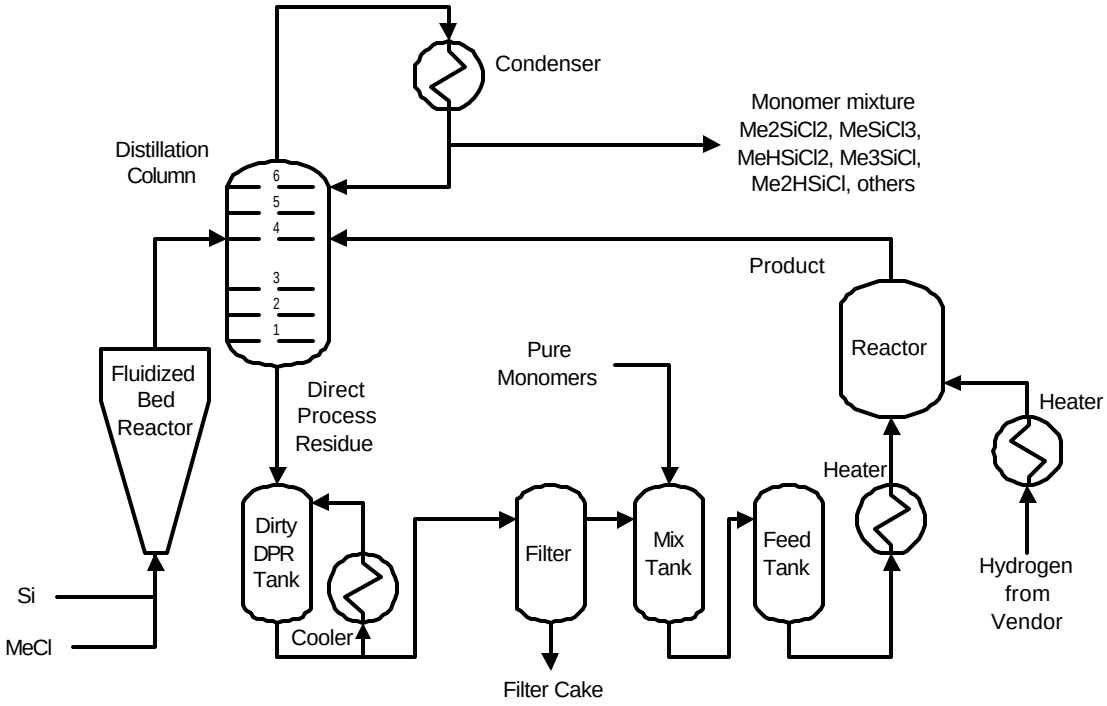
Several hours into the start-up operation, a liquid level forms in the bottom one-third of the reactor vessel. H_2 feed bubbles up through this reacting liquid. Pressure is controlled in the vapor region above the liquid. When pressure rises in the reactor, the reactor overheads pressure control valve opens to lower the pressure. Temperature inside the reactor is monitored at three different vertical heights. Temperature is controlled indirectly by adjusting the power input to the entire oil system at the heater. The liquid level in the reactor is monitored by means of weigh cells and a nuclear density meter, but the level is not controlled directly.

Reactor pressure is controlled at the overheads pressure control valve from the reactor. Overhead product is throttled down from reactor pressure to DPR Column pressure. Unreacted hydrogen and vapor chlorosilanes are continuously vented to the adjoining FBR's DPR column. Liquid product from the reactor is throttled from reactor pressure to DPR Column pressure through a level-control valve, and flows into the adjoining FBR's DPR column.

Typically, product is continuously withdrawn overhead from the reactor. Intermittent blowdown of liquid from the bottom of the reactor is necessary to purge the vessel of unreacted high-boilers and polymer/solid that is being formed. During blowdown, chlorosilane feeds are directed to the top of the reactor.

Pilot Plant II product recovery occurs via the adjoining FBR's DPR column, where monomers from Pilot Plant II join effluent from the FBR overhead. Any unreacted high-boilers or polymer that are formed in the reactor exit out the bottom of the DPR column with the rest of adjoining FBR's DPR.

Figure 1: Process schematic for the Direct Process and Pilot Plant II



2. PILOT PLANT II RESULTS AND DISCUSSION

2.1 Operations and Engineering, May 1998 through September 1999

Carrollton operation was sustained throughout May 1998. On line time (OLT) for the month was 90%. This put year to date OLT at 42%. A failure of a vent recovery component in a downstream process shut down the hydrogenolysis reactor for a few days. Availability was 99% with a brief shutdown to build some feed inventory due to poor filter performance. Overall conversion to useful monomers was approximately 62%, including filter cake losses. The stainless steel filters were not changed out during the month. However, the filter system could support only two-thirds of the design capacity when feeding solids-rich slurry. Effort focused on optimizing the liquid rinse. The chlorosilane preheater showed signs of fouling. Quotes were received for doubling and tripling the throughput of the high-pressure feed pump. Evaluation of other equipment, specifically preheaters and hot oil heater, were needed before a rigorous "stretch" option could be considered.

Carrollton's OLT for June 1998 was 37%. This put year to date OLT at 41%. The reactor was shut down on 13 June. This forced an early shutdown requiring reactor head removal. The subsequent reactor wash out was completed without incident.

Chlorosilane and hydrogen preheater elimination trials were completed to support Barry scope reduction. Process operation was demonstrated without either preheater. No changes were observed when the hydrogen preheater was shut down. The shut down of the chlorosilane preheater caused some problems as we lost the reaction on several occasions, since the process becomes much more sensitive to hot oil temperature changes in this mode of operation.

Chlorosilanes were found in the hydrogen preheater during shut down. A Process Change Request was approved to create a vapor lock in the feed line to prevent reoccurrence.

Carrollton 's on-line-time for July 1998 was 0%. This put year to date OLT at 35%. The reactor had been shutdown on 13 June. A reactor wash out and head removal revealed some corrosion to the vessel internals. This corrosion was repaired and the unit was ready for an August re-start.

The Carrollton process was on total recycle for five days at the end of August 1999. Aluminum chloride results were pending. The process ran successfully for two weeks without the nuclear density meter.

Overall on line time for August was 47%. This put year to date OLT at 37%. Start-up after the July shutdown was held up due to delays constructing the new hydrogen feed line and failure of the nuclear density meter (lost 40.5% OLT). 6.5% OLT was lost due to feed pump failure, 4.5% OLT due to leak through of bottoms control valve, and 1.5% due to problems getting hydrogen tank pumps started.

Filter performance improved after shutdown. Two factors may have contributed to the improved performance: 1) rinse pressure and flow were increased; 2) Filters were left to soak in monomer for several weeks during the shutdown which may have removed contamination.

Carrollton's Pilot Plant II broke monthly records for capacity (total DPR and MCDS fed) and reliability (99% OLT) in September 1998. Pilot Plant II operated on total recycle for 15 days before poor filter performance led to changing to MCDS feeds. No DPR column operating issues arose. Aluminum chloride results were pending.

An alternate reactor configuration trial was run successfully for 10 days. Very high hydrogen conversion was achieved, but disilane conversion was lower than desired.

In October 1998, results from Carrollton's total recycle trial were obtained and reviewed with key personnel at Barry and Carrollton. The results, while informative, were inconclusive and an extended total recycle mode of operation was planned for the end of the year.

The hydrogenolysis reactor broke the capacity record for the second consecutive month, and ran at a 72% on-line time. During Carrollton's half-site shutdown, the reactor was able to consume all of the by-product generated by the half of the site that was operational.

Plans for the next Carrollton total recycle trial were reviewed with key personnel at Barry and Carrollton in November 1998. The plan was to make minor piping and equipment changes so that the trial could begin at the first part of January 1999.

The hydrogenolysis reactor operation was interrupted for eleven days during the middle of November because of a mechanical failure. On-line time for the month was only 48%, due to the mechanical failure and repair time.

The Carrollton total recycle trial was delayed in December 1998 due to site vent recovery system performance problems. The problems were expected to be resolved in January with the trial to start following a week later. Preparations for the trial, piping for feeds and sampling, computer control system changes and data collection programs were completed. Pump repair was also completed.

The hydrogenolysis reactor operation was interrupted for fourteen days at the end of December because of a mechanical failure. Urgent attention was required by the manufacturer. On-line time for the month was only 61%, due to the mechanical failure and repair time.

The Carrollton process did not operate in January 1999. Mechanical problems caused the entire month to be lost. Agitator and pump failures and their repair or replacement were the specific causes.

The Carrollton process did not operate in February 1999. Mechanical problems caused the entire month to be lost. A new feed pump was installed, and leak testing was completed in anticipation of start-up. However, the pump's motor had been undersized and was unable to provide the power necessary. The team planned to re-install the original pump for a March start-up.

The Carrollton process was restarted on 07 March 1999 and ran for five days before a process trip in an adjoining distillation column shut down the process. An attempt to restart the process failed due to a plugged hydrogen feed line. Several attempts to clear the plug failed. The reactor was then washed and disassembled. Inspection found a large number of cladding pits that were then repaired using the same welding technique used in July 1998. This pitting indicated that a continuing problem would exist in that vessel. In parallel to the effort to bring the Carrollton reactor back on line, longer term process solutions (reactor operational changes, design changes) were investigated.

The Carrollton process was reassembled in April 1999, but did not perform correctly. Following a week of unsuccessful vendor efforts at the site, an operational plan was developed. The reactor was then started and, as expected, performance was poor. Solutions to improve reliability of the process were developed including block flow diagrams and cost estimates. Process and mechanical research was in progress to select an alternative by mid-May.

A set of six alternatives for long term processing in Carrollton were identified and were narrowed to four flow sheets. These included the extremes of "doing nothing" and operating status quo, to building a new process at the site similar to the Barry design. A spreadsheet was developed to perform yield and net present value (NPV) calculations and was used in the analysis. Evaluations continued with additional support from site engineering. The strategy was to be defined by the end of May.

Five chemical process industry (CPI) cleaning service vendors were contacted who could provide aqueous or chemical cleaning of this and other site reactors. An on-site meeting was held with one. Others desire process samples to define solvent alternatives.

The Carrollton process operated reliably all of May 1999. Due to the changes implemented in April, wall heat transfer and product composition were different than normal. Significant learning took place concerning the importance of many process parameters in this new operating mode.

One alternative for long term processing in Carrollton was chosen from the set of six alternatives identified in April. The agreed strategy was to increase throughput by a factor of four by the end of year 2000. The NPV of the chosen alternative was high despite significant capital investment.

Samples were sent to three CPI cleaning service vendors for testing. We hoped to identify one that could provide aqueous or chemical cleaning of site reactors.

A "Stretch and Reliability Improvement" project was initiated for the Carrollton process in June 1999. Approval of the scope and plan was obtained from the Technology Center and Manufacturing. Process Flow Diagrams were completed and reviewed. Preliminary equipment sizing and Requests For Quotation on heat exchangers, pump, spare hot oil heater and valves were submitted. Piping & Instrumentation Diagrams for the feed system and reactor modifications were completed. A Hazards and Operability study was completed. Materials Of Construction testing of laboratory coupons progressed. See Section 3 for a complete discussion of this project.

Design engineering work proceeded on the Carrollton Stretch project in July 1999. The HAZOP report was issued. Requests for quotation were issued and received for two heat exchangers, two pumps and the high pressure valves. Purchase orders were issued for two heat exchangers and two pumps. Process pressure analysis was 99% complete pending follow-up on two installed pumps. The Business Council reviewed the project and its economics. Approval was received for preliminary funding, with a Board of Directors application for full funding scheduled for December.

The Carrollton "Stretch/Reliability Project" design effort continued in August 1999 with discipline engineers in all areas. Instrument and control valve list was generated, sizing and specification work was in progress. Detailed layout engineering was in progress. A Request For Quotation on the reactor replacement was issued to two firms. One firm returned a quote for 42 week delivery. The Process Pressure Analysis was completed and issued for Phase 1 of the Stretch project. The Technology Package was held up pending completion of the hot oil system analysis. An analysis of line sizes for stretch rates was completed. A report was issued by a Safety Engineering consultant concerning the placement of the loop equipment. Plans proceeded for shutdown, inspection and construction from mid-October through November.

The Carrollton process ran well during August 1999. On-line time was high with small downtime incurred for hydrogen recovery tie-ins, liquid dump valve replacement and preheater cleanout. A "total recycle" campaign was initiated 12 August. No processing issues arose during the month, but frequent filter changes were required. A written proposal was received for reactor cleanout from a waste management company. Another company was completing some corrosion testing and would issue their quote by mid September.

The Carrollton "Stretch/Reliability Project" Technology Package for Phase 1 was completed, approved and accepted in September 1999. A review of the project selection and scope was completed during the Technology Center monthly meeting. No changes were identified to the path of stretching over three phases. The Safety Audit Team chairman held a first organizational meeting to review technology and project scope. The detail design and construction packages were over 75% complete. Nine engineers in Plant Engineering were actively working on the project. The second quote for the reactor replacement was received. The second vendor's quote was 5% higher than the first's. We chose to proceed with the first vendor for reactor vessel fabrication. The

vessel cleaning contractor for the shutdown was selected pending completion of the vendor qualification package.

The Carrollton process ran well during September 1999. Six days down time were experienced due to the high pressure feed pump gearbox failure. Good performance of the vapor analyzer was observed after the capillary column was replaced with a packed column. Good conversion to high-value product was achieved during the "total recycle" feed campaign, which was planned to continue until the November shutdown.

2.2 Pilot Plant II Material Balances

Table 1: Hydrogenolysis Material Balance

		Month1	Month2	Month3	Month4	Month5	Month6	Month7	Month8
Feeds	DPR	80	47	33	39	16	41	13	73
	MCDS	113	53	73	217	248	129	206	100
	Monomer 1	103	51	37	79	41	24	26	133
	Monomer 2	29	22	18	34	28	18	24	29
	H2	4	1	1	3	5	3	4	4
Products	Monomer 1	136	70	59	137	119	25	63	196
	Monomer 2	76	50	47	114	147	110	129	1
	Monomer 3	15	6	8	13	10	2	4	57
	Monomer 4	12	4	6	11	10	2	4	1
	Monomer 5	11	5	11	17	22	54	38	14
	DPR	61	30	23	67	22	10	30	47
	Filter cake	18	11	8	12	8	11	7	15
DPR Conversion		59%	60%	71%	69%	89%	88%	83%	65%

The mass-balance table shown above gives a dimensionless analysis of the Hydrogenolysis Process performance for eight representative months during May 1998 through September 1999. Overall conversion of high boiling feed is calculated as …..

$$X_{reactor} = 1 - (m_{filter\ cake\ +\ unreacted\ DPR} / m_{feed\ DPR\ +\ MCDS}).$$

2.3 Reactor Cladding Pitting Issues

2.3.1 Introduction

The Carrollton process reactor has been inspected twice since it was placed in service in October 1997. Both inspections, July 1998 and March 1999, revealed pitting of the Inconel 625 reactor cladding. The pitting was hypothesized to have occurred either during normal operations at high temperature and with metal chlorides present, or during periodic caustic soda washing to remove chlorosilanes and solid residues. A laboratory experiment was therefore initiated in effort to determine if pitting of the cladding could occur under anhydrous normal operational conditions.

The purpose of the experiment was to evaluate the effect of high temperature and hydrogenolysis chemical environment (hydrogen, disilanes, methyl DPR high boilers and metal chlorides) on metal coupons and determine if metal pitting will result under these conditions. Metal coupons were obtained from an exotic metals supplier. The coupons purchased included 316L, Hastelloy C276, Inconel 625, a VDM Alloy, and Inco 800HT. These selections were made to evaluate a full range of materials, to include ones that were expected to pit.

2.3.2 Discussion

Following exposure of the coupons to the hydrogenolysis chemical environment at high temperature for 408 hours, no weight loss was observed compared to initial coupon weights. All coupons were evaluated under a 30 power stereo microscope. No pitting was noted on any of the coupons. The 316L sample was examined in a Scanning Electron Microscope and compared to a virgin 316L coupon. No pitting was identified.

The lack of pitting in the laboratory after 408 hours of exposure can be contrasted to the severe pitting in reactor coupon samples that had been in service from October 1997 through July 1998 in the Carrollton reactor.

When reactor coupons were installed for nine months (Oct97-July98) it has previously been estimated that the reactor was at process conditions for 3240 hours during that time. Reactor temperatures commonly employed were mild. During this time frame there were four reactor cleanouts that used water and caustic solution.

The laboratory system was in service 408 hours and was maintained at temperatures about 100 degC higher than the reactor temperature during the nine month period cited above. The intent was to subject the laboratory coupons, for a shorter time, to higher temperature than the reactor coupons.

The reactor coupons underwent four cleaning cycles. A typical reactor cleaning cycle is to vent, cool and drain the reactor to the DPR column. In some cases a polydimethylsiloxane fluid rinse is completed. A bottoms connection and overhead vent connection to a scrubber are installed. The reactor is slowly filled using a caustic and water solution. In most cases the reactor will not be completely filled (at times as little as 100 gallons was used). The reactor will typically exotherm with fluid temperatures reaching 100C. The slow addition of the caustic solution is required due to the foaming that occurs upon H_2 and N_2 evolution.

Following caustic wash the reactor is filled with water several times and drained. At this time the reactor head may be removed for maintenance inspection or the reactor returned to service. Head removal may take more than ten days due to bolt removal problems, equipment scheduling, etc. If the reactor is returned to service it will first be rinsed with chlorosilane monomer to remove all water.

It appears possible that the aqueous wash techniques employed may be causing the pitting. Likely contributors are

- the slow addition of the caustic,
- failure to hydraulically fill the reactor,
- the long time that weak acids - including non submerged areas, poorly agitated zones and acids trapped under solids - may be in the system prior to head removal and water blasting.

Service contractors have been identified that could provide cleaning techniques that supplement our in-house methods. Their equipment includes pump trucks and tank trucks. They also employ corrosion inhibitors, surfactants and other additives. One such contractor's proposal is to

hydraulically fill the reactor with a low strength caustic solution, to reduce foaming. The reactor would be vented back to the tank truck where foaming is controlled (larger diameter pipes and antifoam agents). The tank will also be cooled with internal coils. Then the caustic solution would be recirculated at a 600 GPM rate for over 400 volume changes. Caustic strength is monitored and rejuvenated as required. Then use other chemical additives to clean residues (these materials were identified during lab testing by the vendor on hydrogenolysis solids samples). Finally using a rotojet type water blaster, enter the top nozzle and jet blast the interior. This is clearly different than the in-house technique; the vendor would hit the vessel "hard and fast" with caustic with one-hundred-fold more volume changes that we have in the past. Additionally, Dow Corning maintenance personnel need to have new tools in place that will allow for more efficient head removal to shorten the time requirements significantly.

2.3.3 Coupon Exposure Protocol (Laboratory)

Place metal coupons in 600 ml Parr lab reactor. Coupons held in place vertically around circumference of reactor by specimen holder. Reactor filled with 126 gm DPR filtrate obtained from Carrollton Manufacturing. Add an additional 3.5% metal chloride to the reactor to increase the fraction and the potential effect of metallic salts. Pressurize lab reactor to 40% of plant reactor pressure at ambient temperature with hydrogen. Heat reactor to high internal temperature. Pressure increased beyond operating pressure and was bled down. Temperature was maintained for 17 days (408 hours). Reactor pressure was bled off twice more and was maintained within +/- 50 psig of normal operating pressure during the course of the run. Vent reactor to dry ice chilled bomb. Allow reactor to cool and remove from mount [5].

The coupons were then removed. Photos of reactor and coupons rack indicate that significant solids were present; see Figures 2 and 3. Solids collected weighed 9.2 grams (7% of material added to reactor). Solids were also bound to the metal coupons.

Figure 2: Parr Reactor (solids inside)

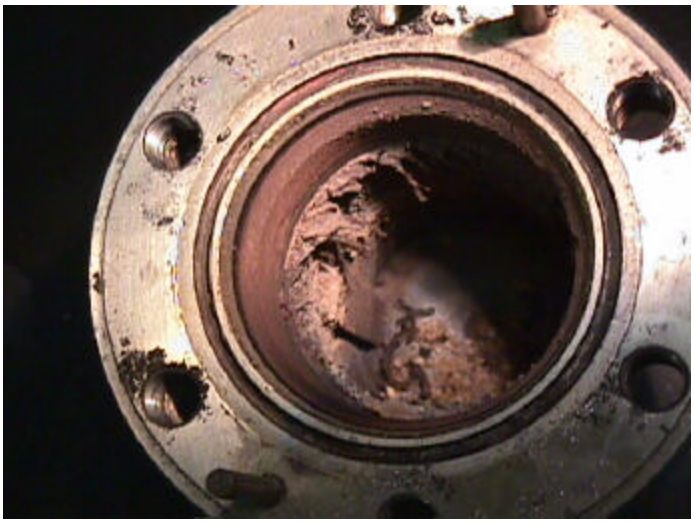
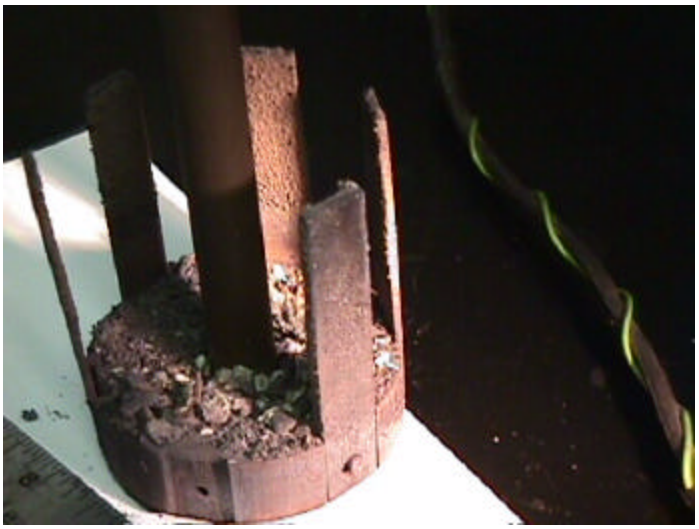


Figure 3: Solids adhere to Coupon Rack following reactor evaluation



Coupons were placed in 15% KOH solution. A magnetic stirrer was used to agitate the solution. The bath was replaced three times over a five day period. The coupons were taken to an inspection firm for weight loss analysis and surface inspection.

2.3.4 Future Work

The Carrollton plant reactor will be inspected again in November 1999. New alloy coupons had been placed in the reactor in March 1999. These will be examined by a consulting firm at that time.

2.4 Pilot Plant II Safety Incidents

Since the previous technical report, there have been six spills or leaks, two fires or smolderings, two near-misses, and one relief valve lifting. None resulted in personal injury. Summaries of some of the incidents follow [6].

2.4.1 Spill and smolder, 05 April 1998

Technicians were heating up the reactor after maintenance to pressure test the reactor. While heating up, some removable insulation started to smolder. The insulation was found to be contaminated with oil from a leaking fitting above the insulation. The reactor was cooled down to replace insulation. A leaking fitting caused the spill, resulting in smoldering insulation when heated up.

2.4.2 Spill and near miss, 18 August 1998

A technician was starting up the high-pressure feed pump to provide feeds to the reactor. The technician started the pump and then moved to the side to observe the discharge pressure gauge. When the discharge pressure was within 50 psi of the reactor pressure, the gasket on the discharge flange connection of the pump failed and feed material began to spray from the flange. The technician immediately shut the pump down and stopped the leak. The technician was not in front of the gasket failure and was unharmed. It was later discovered that a bolt on the flange was loose, which caused the failure. Leak testing the connection prior to start-up had not been completed; this would have revealed the loose connection.

2.4.3 Spill and near miss, 07 October 1998

The technicians were starting up the high-pressure feed pump after maintenance. The piping was pressure checked on both suction and discharge sides. When the discharge pressure reached half the reactor pressure, material began to spray from the check valves on the pump. The outside technician contacted the control room and the pump was shut down remotely, stopping the leak. No one in the vicinity of the pump was struck by the material that sprayed out. Mechanical failure was the proximate cause.

2.4.4 Fire, 10 November 1998

The reactor had been isolated and was being prepared for maintenance. The reactor pressure had been vented down and the next step was to remove a blind flange on the reactor vent line and install a hose that would allow the reactor to be connected to the venture scrubber so that it could be purged. The technician loosened the blind flange and allowed the pressure trapped in the three-foot spool piece downstream of the valve to bleed off. The technician then removed the blind flange. When the flange was removed a "puff" of fire shot from the end of the pipe and immediately went out. The technician then notified the Site Supervisor of the fire. The proximate cause of the incident was the leaking isolation valve, with the presence of the extension spool being a contributing factor.

2.4.5 Analyzer relief lifted, 13 December 1998

During normal operations the vent compressors for the hydrogenolysis process, shared with an adjacent process area, shut down unexpectedly. This event automatically initiates a hydrogenolysis process shutdown. The overhead analyzer relief on the hydrogenolysis process lifted, causing a small release to the vent stack. The analyzer was valved out, stopping the release.

2.4.6 Pump seal leak, 16 February 1999

A technician was making a routine process check and found a seal leak on the filter feed pump. The pump was shut down and valved out, stopping the spill. Mechanical failure was the proximate cause.

2.4.7 Valve stem leak, 06 September 1999

While making rounds, a technician discovered a leak on the filter cake dump valve. The valve appeared to be leaking from the stem and had accumulated a ball of gels there. The technicians shut down the filter and prepared the valve for replacement.

2.4.8 Hydrogen leak, 14 September 1999

Personnel in the vicinity of the liquid hydrogen tank heard a loud "pop" followed by a high pitched noise indicating a high pressure leak. A leak was discovered on the hydrogen equipment inside the vendor-leased fence-enclosed area. The exact source of the leak could not be determined and emergency shut off for the skid was activated. All employees were removed from the area of the skid and surrounding roads were blocked off. A notification call was placed to the vendor asking them to respond to the site. The leak continued for approximately 1.5 hours until the vendor's technician arrived. The pressure from the leak was noticeably decreasing during this time. When the technician arrived he entered the fence-enclosed area and shut isolation valves to stop the leak. The source of the leak was discovered to be a ½ compression fitting on the pump discharge pressure tubing that had become disconnected. The tubing had blown out of the tee. The leak resulted in almost the entire contents of the high pressure surge system being released. The technician repaired the tubing and the system was placed back into service.

3. PILOT PLANT II STRETCH

3.1 Project Description

The project objective is to 'stretch' the capability of the Carrollton hydrogenolysis process four-fold. The focus will be on feed capability, reactor capability, reliability and future stretches. The reactor feeds will increase four-fold. The reactor volume will be increased by 90% to accommodate higher rates. The reactor will be replaced with an alloy clad metal and an external pump loop will be added to allow the reactor heat input to be from an external heat exchanger. The pump loop will allow efficient operation and allow for the reactor internal diameter to be increased (by eliminating the need for a jacket) while remaining in the existing tower structure. A second flow path on the pump loop will allow for the piloting of alternative reactor designs and provide stretch options.

Due to equipment order lead times the project will be divided into three phases. The phases are described below.

Table 2: Pilot Plant II Stretch Milestones

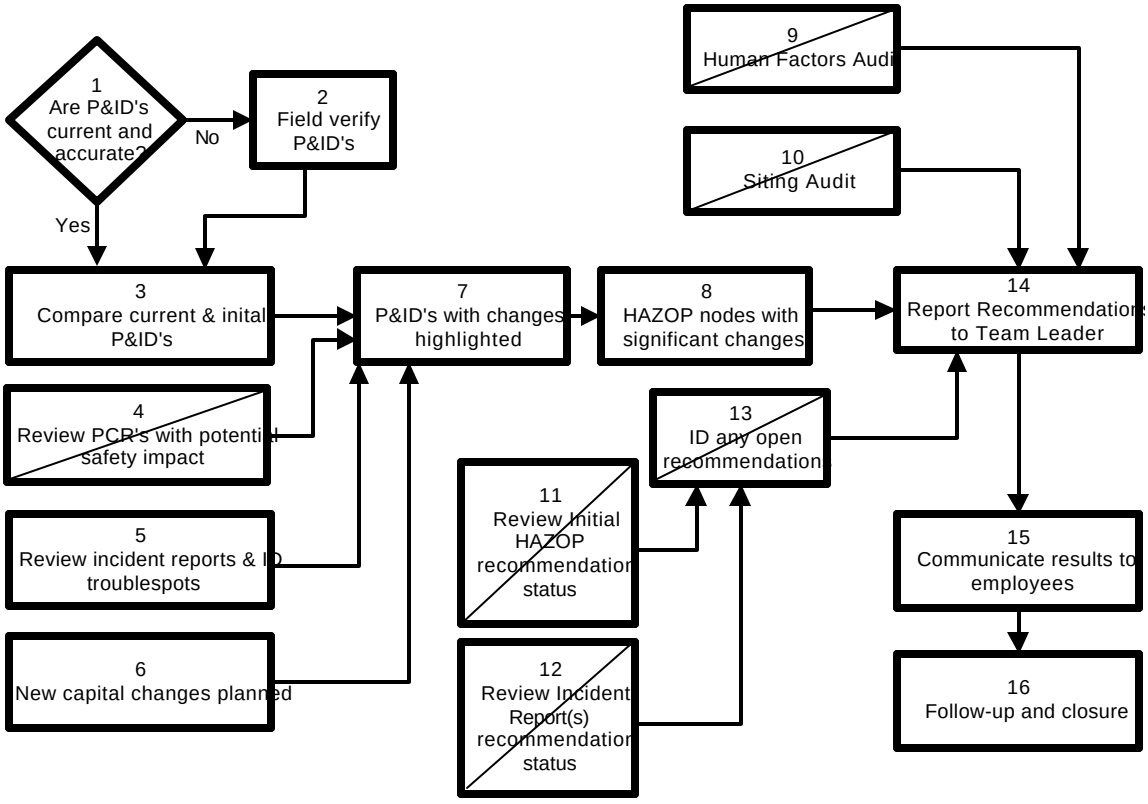
Phase	Timing	Description
1	Oct 99	Replace high-pressure reactor-feed pump and chlorosilane preheater, modify monomer feed locations, install reactor primary loop and heater
2	Apr 00	Install auxiliary reactor loop
3	Sept 00	Replace reactor, upgrade hot oil system if necessary

3.2 Process Hazards Analysis

3.2.1 Introduction

The Hydrogenolysis process contains hazardous materials above the threshold limits set forth in Dow Corning Corporate Safety Health &Loss Prevention Standard, "*Process Safety Program.*" This section documents the Process Hazard Analysis (PHA) for Pilot Plant II Stretch [7]. Steps numbered 1, 2, 3, 5, 6, 7, 8, 14, 15 & 16 are part of this study as shown in the figure below. As will be discussed in Sections 3.2.8 and 3.2.10-11, prior work had eliminated the need for duplication of some of the steps in the PHA revalidation process. After confirmation by the PHA leader and project coordinator, these steps were not repeated as part of this effort. The workflow is referenced in the site *Process Safety Manual* and is shown in the following figure, with single-line strikeouts through the previously performed steps.

Figure 4: The PHA Revalidation Process



The Study used the line-by-line Hazard and Operability Study (HAZOP) method of analysis, reviewing a set of deviations for each node. A node is grouping of process lines and/or equipment. HAZOP software developed in Microsoft Access was used for this PHA Revalidation.

3.2.2 Objectives

- Ensure that the Project PHA is consistent with the current process configuration and technology,
- Identify known hazards,
- Ensure that adequate controls are in place (and being maintained) to help prevent or mitigate identified accident scenarios,
- Consider human factors, facility siting, and the function of the emergency shutdown system, (Note, human factors, facility siting were studied in the 1996 study and are not being restudied at this time)
- Meet Dow Corning CSH&LP requirements set forth in “Process Safety Program” “Hazard Evaluation Techniques” standards.

3.2.3 Assumptions

Based on experience, the PHA team made several assumptions prior to conducting the revalidation. These assumptions were not discussed in detail during the revalidation, except as noted below or if dictated by concerns or legal/insurance requirements. Overall, this allowed the team to focus on areas with potentially higher levels of risk.

- Electrical and air supplies to instruments are reliable.
- Manual valves which meet Dow Corning piping specifications are reliable.
- Piping is reliable when it is agreed that the specification is correct.
  Where corrosion, erosion, or lining failure is known or expected to occur, the team discussed leak potential, material selection, and other means of protection.
- Leaks are assumed to occur only at piping joints. These leaks could have serious consequences of spilling or releasing hazardous materials.
- The site Emergency Response team will take immediate action to stop spills and releases.
- Containment of spills is within appropriately diked areas.
- Utilities are reliable.
  Utilities are discussed only if they are considered to be critical for process control, such as a dedicated cooling system on an exothermic reaction process.
- The system is dry before process materials are introduced.
- Potential process contaminants will be [heat transfer fluids, water, refrigerants, etc.].
- Winter bypasses on water/condensate systems are used per the SOP to avoid freezing problems.
- Three levels of protection are required. These levels are:
  - ⇒ Basic instrumentation with alarm limits that can be set by the [Technician/Operator].
  - ⇒ A dedicated instrumentation and alarm system for safety interlocks or an Emergency Shutdown system.
  - ⇒ A Mechanical Integrity program which ensures the integrity of the process. The process is assumed to contain material during normal operation and during shutdown.
- Pressure relief systems for fire exposure venting have been designed and installed properly.
- Fires under flammable storage tanks have been addressed in engineering design and pressure relief system design scenarios.

3.2.4 Recommendations Management

Recommendations were developed as a result of this PHA. Safety and environmental recommendations were risk ranked by the PHA team based on estimates of *probability* and *severity* using the site Risk Ranking Matrix. Other recommendations were not risk ranked. The Project Coordinator ensured that the recommendations were properly entered in the Recommendations Management System (RMS). The Project Coordinator will manage these recommendations to resolution in a timely manner and prior to startup of the new facility. In consultation with the Manufacturing Engineer, the Project Coordinator reviewed the recommendations with personnel whose jobs may be affected by them.

3.2.5 Process Description of Changes

The purpose of the Phase 1 Stretch Project is to increase the ability to feed material and address corrosion problems with the reactor.

The operational philosophy for the stretch process will be to make only minor modifications to the filter system. The modifications will allow for more efficient materials handling in the filtrate tank and reactor feed tanks but will not change the filter feed tank or the filter. The process will be operated to filter as much DPR as possible and make up for the remainder of the feed stream with MCDS overheads. The MCDS column will be operated to control the solids level in the still pot with the remainder being taken overhead. This is a change from the current operation that controls the side draw at a low level of high boilers in that product stream.

The Stretch Project will also add a recirculation loop to the reactor. This will allow for heat transfer to the reactor to occur in a shell and tube exchanger rather than through the vessel walls. This should reduce corrosion on the vessel walls.

A description of the changes to the process during Phase 1 is as follows.

- DPR Tank - No MCDS will be fed to the DPR tank or processed through the filter.
- Filtrate Tank - Filtrate accumulates in this tank and is mixed with clean MCDS from the tank farm; no longer will it be mixed with monomer here.
- Reactor Feed Tank - During the transfer cycle from the filtrate tank to the reactor feed tank, monomers are ratio-mixed in a static mixer with the MCDS/filtrate from the filtrate tank. This mixing provides a completely mixed stream which is ready to feed to the reactor.
- Pump loop - The Reactor has an auxiliary pump loop where the contents of the reactor are pumped through a heat exchanger, which provides the make-up heat for the endothermic reaction, and then back to the top of the reactor. The pump loop serves two purposes. First, the fluids are heated outside of the reactor with a heat exchanger instead of inside the reactor by a jacket. This outside heating maintains the reactor's walls at a relatively low temperature, which prevents corrosive pitting from occurring. Secondly, the pump loop recirculates solids, helping keep solids from building up inside the reactor. Periodic liquid purges allow the suspended solids to be removed from the system.

3.2.6 Process Hazard Identification Summary

The study is based on:

- A project addition to the prior total process PHA
- A project update of the P&IDs
- A review of relevant Process Changes and Projects
- A review of accident history since the last PHA as relevant to the project changes
- Consideration of incident scenarios with potential off-site impacts

3.2.7 Process Hazard Identification Scope

Details of the various assessments and reviews follow. Based on the results of these efforts, the overall scope of the study can briefly be stated as follows:

- Only Project changes have been studied in this HAZOP. This is Phase 1 of a three phase project which will have separate HAZOP studies and reports. An overall HAZOP Revalidation should be performed in 2001, after the project is completed and piloted for one year. The overall revalidation can tie all the project changes and the ongoing needs together.
- This Phase 1 HAZOP is a study of chlorosilane feed system changes as well as the addition of a pump and heat exchanger recirculation loop to the reactor.

3.2.8 Assessment of Prior PHAs

Available information from all prior PHAs and mini-HAZOPs was assessed before conducting this study. A PHA had been conducted in August 1996 on the original installation of the Carrollton hydrogenolysis process.

It was determined by PHA Leader and the Project Coordinator that a PHA study of the project changes, rather than a completely new PHA, was sufficient to meet the stated objectives.

Table 3: Table Piping and Instrumentation Diagrams

Drawing Number	Drawing Title
16	FILTRATION
17	FEED SYSTEM
18-1	REACTOR
18-2	PREHEATERS
19	HOT OIL SYSTEM
37	ESD LOGIC TABLE
91	RECIRCULATION LOOP
97	PROCESS INTERLOCKS

P&IDs used during the Study were clearly marked, showing accident locations, node definitions, and the endpoints of the study. Blue marks were used on a copy of previously reviewed P&IDs to indicate equipment that had been removed. These copies were not retained for the record since the P&IDs studied indicated all removals. Minor errors discovered during the study were also noted on the P&IDs. These errors were corrected by the Project Coordinator and were not specifically noted in the recommendations.

3.2.9 Reference PHA Studies

The P&IDs were also checked to ensure that all process lines and equipment were either covered by this PHA or another PHA. There were no lines leaving or entering this process to be cross-referenced with another study.

3.2.10 Process Change Requests

A study of process change requests (PCRs) was not performed with this project HAZOP study, because all changes due to PCRs were accurately reflected in the P&IDs.

3.2.11 Projects

There have been no projects since the original HAZOP which were not covered by PCRs. Therefore there was no need to review any prior projects for their contribution toward process hazards.

3.2.12 Five Year Accident History

A summary of the spills, releases, fires, and injuries that have occurred since the last PHA and which impact the three nodes under study was reviewed.

3.2.13 Trouble Spots

Discussions with HAZOP Team revealed the following trouble spots as a result of their knowledge and experience. The conclusions from these discussions impact on the scope of the study as follows:

High Pressure Feed pump Gasket on ball check valve failed. Near miss incident with operator. Flange failure resulting in near miss with operator. New pump being purchased.

Reactor Noticeable pitting since initial start-up. Required welding repairs every 4-6 months. Pitting seems to be caused by high wall temperature being reacted with settled solids on the wall. New material of construction is needed. This project will remove heat from the wall of the reactor.

3.2.14 Potential for Off-Site Impact

PHA recommendations were risk ranked, with a *Very High* severity corresponding to the potential for an off-site impact. In essence, the PHA team considered the potential for off-site impacts throughout the study. An incident scenario is like a script. It may or may not have happened. In fact, the Process Safety Program is designed to prevent or mitigate the effects of incidents and off-site impacts. The PHA team and the Process Safety Coordinator developed two realistic incident scenarios that could potentially result in off-site impacts, as displayed in Table 4. This discussion was based on their process knowledge and experience, and the reasonable likelihood of this type of event. This list may be amended during subsequent PHA Revalidations.

Table 4: Incident Scenarios With Potential Off-Site Impact

Scenario	Amount Released, Duration, and Area Affected	Basis for Selection	Conclusion
Failure due to corrosion in 2" line from reactor to DPR Column	Ladder and Breathing Air required to shut off the flow. Column would have to vent to atm pressure. Liquid and solid material contained inside the process area.	Postulated probability of occurrence, and severity of off-site impact	Not likely to happen and would have significant off site impact (vapor cloud).
Corrosion or mechanical force causes 1" line failure southeast of Tower	**100 gallons of monomer released over 10 minutes.** Liquid material contained inside the process area.	Postulated probability of occurrence, and severity of off-site impact	Not likely to happen and would have minimum off site impact.

3.2.15 Node Definitions

To meet the objectives and satisfy the scope of the revalidation, nodes were defined as follows.

Table 5: Node Definitions

Subsystem	Description Of Change NDS = Not Deemed Significant	Decision For Study
Filtration	Added Me2SiCl2 line to flush Filter Removed cooler	Node 3 NDS
Feed	Added MCDS feed to filtrate tank Removed monomer feed from filtrate tank Added monomer feed to reactor feed tank	All in Node 3
Reactor	Removed Nuclear Density Meter from reactor Added hot oil and recirculation connections to drawing 97	NDS Node 1
Preheaters	Changed chlorosilane preheater to shell & tube and added bypass Added H_2 connection to chlorosilane feed line. Split hot oil supplies to preheaters & reactor.	Node 2 Node 2 NDS
Hot Oil	Split hot oil supplies to preheaters & reactor.	NDS
ESD Logic	Updated ESD Matrix for project	ESD
Recirculation Loop	New pump loop	Node 1
Critical Interlock Logic	Updated Interlock Dwg for project	ESD

3.2.16 Recommendations and Follow-up

Twelve recommendations resulted from the three-day study. Two recommendations were the result of Very High Risk process deviations; five were the result of Medium Risk process deviations; one was the result of Low Risk process deviations; four stemmed from non-safety-related deviations which were not risk-ranked. The two Very High Risk deviations and the resultant recommendations are as follows.

Table 6: Very High Risk Process Deviations

Deviation	Cause description	Consequence description	Consequence	Recommendation	Responsible person
Thermal shock or expansion	loss of cooling to recirculation pump, or loop valve closed with hot oil still on	pump failure or flange leak	spill	lock open the valve between the new heat exchanger and reactor	Manufacturing Engineer
Thermal shock or expansion	monomer feed lines are not protected for thermal expansion	on shutdown, these lines will be stressed and leak	spill	assure that the monomer lines are blown dry when shutdown to avoid leaks from thermal expansion	Manufacturing Engineer

These two "very high risk" recommendations, and all others, will be addressed in a timely manner prior to the commissioning of the process changes.

3.3 Fire And Explosion Safety Study

A Fire and Explosion Safety Study was conducted by an outside consultant, specifically for Pilot Plant II Stretch [12]. The following topics were investigated, discussed and suggestions made.

3.3.1 Circulation Pump Location

Part of the stretch project is to change from jacketed heating to an external loop with pump, heat exchanger, and other necessary accessories. The pump would handle a mixture of combustible liquids at high pressure and temperatures above the flash points of the components.

1. Ground floor - installing the pump on the ground floor could create a hazard to the cable trays and pipe racks overhead, in the event of leakage of the flammable liquid and ignition. Installation of pumps under cable trays is not recommended.
2. Second floor - installation and maintenance would be more of a challenge with a second floor installation. A monorail, trolley and hoist would probably be required. Pump leakage and fire would be a less serious hazard here, however, than with the ground floor installation. The second floor installation is recommended.

3.3.2 Heat Exchanger Location

The proposed third floor location is appropriate.

3.3.3 Fire-Resistant Clothing

1. Type of clothing - the uniforms presently available for employees and visitors is reportedly quite uncomfortable to wear in hot weather. Several alternatives were suggested.
2. It was suggested that the locations requiring fire-resistant clothing be limited to:
    - areas of restricted egress
    - vicinity of equipment containing hydrogen
    - vicinity of equipment containing fluids above the autoignition temperature
    - the top of the reactor

3.3.4 Other Aspects of the Process

1. Relief discharge piping - at least four relief system discharge pipes vent horizontally from the top of the process tower. It is generally recommended that discharges be directed vertically to minimize reaction forces and provide maximum dispersal of toxic and/or flammable materials.
2. Monitoring of the rupture disk/relief valve space - routine inspection of pressure gauges installed between rupture disks and relief valves is considered too infrequent. Installation of pressure switches that alarm the process control system is recommended.
3. Hydrogen supply - the liquid hydrogen tank is isolated from the rest of the plant and is unlikely to cause damage to the plant in the event of fire or explosion. However, better preparedness for a hydrogen leak emergency is needed. The push button near the hydrogen facility should be labeled to describe its function, which is to shut off the supply of hydrogen to the process tower. The hydrogen supplier should periodically test the emergency shutdown system. It may be advisable to conduct a Process Hazards Analysis on this facility.
4. Hydrogen leak detection - since hydrogen burns with an invisible flame, providing devices to provide early warning of hydrogen releases, identify the location of leakage, and/or aid in emergency response activities should be discussed.
5. Protection of heat exchanger shells from over-pressure - the shells of the hot oil-heated exchangers are not rated for the tube-side pressures. "Dynamic-response" calculations are recommended to determine if a tube rupture would subject the shell to pressures above the design pressure, as a result of the "inertia" of the hot oil in the piping to the vented storage tank.

3.4 Process Pressure Analysis

Due to the nature and scope of Pilot Plant II Stretch, a process pressure analysis (PPA) was required [8]. A PPA considers each piece of equipment in the system. For each piece of equipment, a "what-if" scenario is considered to determine potential process upsets and likely consequences to the equipment. The maximum process pressure is selected from the scenarios considered. The design pressure is calculated from this maximum as described in Dow Corning's Project Design Manual [9].

3.4.1 Possible Upsets to Consider

1. Improper Ratio of Feeds
2. Excess Reactants
3. Dead-heading or plugging
4. Consider the vapor pressure of all liquids
5. Pump or Compressor Failure
6. Utility Loss
    - 6.1. Electrical
    - 6.2. Instrument Air
    - 6.3. Nitrogen
7. Heat Removal or Addition
8. Clearing plugged lines
9. Other pressure scenarios

3.4.2 Determining the Equipment Design Pressure

The maximum process pressure (MPP) for the design basis is selected from upsets listed above. The Maximum Allowable Working Pressure (MAWP) is then calculated as a function of the MPP. Based on the value of the MPP, the calculation of the MAWP varies. For example, at an MPP less than 50 psig, MAWP = MPP + 10 psi. If the MPP is between 1000 and 5000 psig, the MAWP = 1.1 x MPP.

3.4.3 Conclusions from the PPA

1. Pressure from the monomer supply lines (up to 200 psig) is adequately guarded against by multiple levels of overfill/over pressure protection. A lower maximum design pressure of 90 psig for the reactor feed tank is warranted.

2. Protection from high pressure from bottled gas used for clearing plugged lines (or possibly even from pneumatic leak testing) cannot be designed into the equipment. Adequate safeguards have been used in the past and must continue to be provided in operating procedures and gas delivery system designs.

3. The reactor feed tank and the chlorosilane preheater have a potential for over pressure situations due to their links to the positive displacement pump. They are protected with multiple relief valves (internal pump, pump discharge and tank) and overfill protections. It was appropriate that the design basis for the reactor feed tank should be 90 psig (maximum operating pressure; nitrogen line pressure) and the design basis for the preheater is the pump internal relief pressure.

4. Protection against liquid thermal expansion is provided at the chlorosilane preheater in the case where the heater is manually blocked closed or shut down while operating. The oil flow is interlocked to shut down with low chlorosilane flow thus preventing thermal expansion or boiling in the preheater.

5. Tube rupture of the hydrogen preheater and chlorosilane preheater and wall rupture of the reactor which allows high pressure fluids to enter the hot oil system is a remote possibility. Design of the hot oil system pressure alarms, operating procedures, inspections and relief valves address these scenarios.

6. Although slightly below the 1.25 x Max pressure guideline, the existing DPR tank, filtrate tank and reactor feed tank are adequately protected against pressure to allow MAWP of 110 psig where a potential exists of pressurization from the 90 psig nitrogen supply header due to relief valves in the site nitrogen header system.

3.4.4 Recommendations from the PPA

1. The filter high pressure alarm should be interlocked to turn off MCDS supply valve. If the MCDS pump operates against a shut-off head, it would activate the filter high pressure alarm and should be interlocked to shut off the MCDS supply to the filter.

2. The pressure rating for the process heaters and reactor are being reduced due to the experience gained from the first 18 months of Carrollton operation. Therefore the trip points around the reactor feed pump will be changed. The new pump design will make this possible. Process interlock pump high pressure will trip at 1.2 x reactor normal operating pressure to close the feed block valve and shut down the pump. The new reactor feed pump should be specified with an internal relief inside the pump at 50 psi greater than this. The external relief should be set at yet

another 50 psi higher than the internal relief. This relief is piped back to the pump's supply tank. The preheater's rupture disk and relief should be set at 1.5 x normal reactor operating pressure.

3. Interlock the reactor recirculation pump status to the loop heater hot oil flow. This will ensure that no oil flow is sent to the loop heater if the pump is not recirculating.

4. Current temperature Emergency Shutdown (hardware) Level 3 System (ESD), Emergency Shutdown (software) Level 2 System (ESS), and Process Interlock Level 1 System shutdowns begin at temperatures used in the original hydrogenolysis design. Operating experience has shown that the reactor can be operated 100 degC cooler than first expected, and the hot oil loop 75 degC cooler than first expected. Therefore the conditions should be changed for a ESD reactor and oil trip.

3.5 Basis of Design / Performance Specification

3.5.1 Rate

The Carrollton Hydrogenolysis Stretch was asked to accommodate a four-fold increase in the DPR feed stream. The assumptions included that the majority feed stream would be an MCDS column side draw with the column operating with a 30% solids slurry bottoms stream, that the DPR production rate is 2% of Process A Crude, and that the solids blow over (impacts MCDS column bottoms solids level) is 1% (i.e., 1% of silicon fed to FBRs is blown past the cyclones to the DPR columns).

3.5.2 Conversions

Conversions in the Carrollton Hydrogenolysis reactor were assumed to be 92% for disilanes, 50% for silmethylenes, and 25% for high boilers.

3.5.3 Reactor Size

Reactor residence time to meet the required conversions is assumed to be half of the original design. This is based on operational data from the existing reactor. An evaluation of the existing structure was made and it is estimated that the reactor diameter could be increased about 20 percent without changing the existing steel and about 40 percent if the supporting I-beams were modified. The plan is to provide the maximum diameter which allows for straight forward installation of the reactor (considering side mounted manway interference). The vessel length will be increased by about 17 percent. There is some uncertainty about the reactor vessel contents density, and maximizing the vessel volume will ensure that the design rate will be achieved. The initial quote request will increase the volume by 90% over the existing vessel.

3.5.4 Feeds

To meet the production rate requirements the stretch will provide a reactor feed capacity four times its current capacity (expected mix is 50% DPR/MCDS and 50% monomers).

3.5.5 On Line Time

The process should maintain an approximate on-line time of 6800 hr/yr. This includes a 4 week shutdown and 85% OLT outside of the shutdown window (average OLT for year 78%).

3.6 Critical Design Criteria / Technology Issues

3.6.1 Reactor Pitting

Reactor pitting has been a significant issue in the current reactor. Two vessel inspections have been conducted since the process was started up in October 1997. Both inspections showed pitting. The pitting tended to occur on the vessel bottom and at the liquid/vapor interface under a solids buildup. The current vessel is clad with Inconel 625 and circulates hot oil through the reactor jacket. The new reactor will be clad with a VDM Alloy and be outfitted with an external heat exchanger for supplying heat to the process. Both of these changes could provide reduction or elimination of vessel pitting. The current vessel reliability is reduced due to frequent inspection which require removal of the vessel head. Removal and reinstallation of the head has been a lengthy process (> 6 weeks). The new vessel will have a manway which will be easier to remove.

During Phase 1 of the project the current reactor will be modified. The modifications are intended to assist in maintaining solids in suspension, which then allows the solids to be purged during liquid dumps.

3.6.2 Pump Loop

The reactor pump loop will provide both agitation and heat transfer (through an external heat exchanger) for the reactor. Selection of the pump and heater should focus on reliable hardware.

3.6.3 Chlorosilane Preheater

The current preheater supports very low fluid velocities and can tend to foul. The new heater should be multiple pass and provide higher tube velocities.

3.7 Process Chemistry

No new mechanisms for molecular-level chemistry have been proposed since the Department of Energy Technical Annual Report published in October 1998, as described in the Preface of this report [13].

4. BARRY FULL-SCALE DESIGN

4.1 Engineering, June 1998 through September 1999

Design efforts for the Barry unit during June 1998 focused on completing the Front End Package and finalizing the Capital Cost Estimate.

The focus in Barry during July 1998 continued to be scope reduction to reduce the capital cost estimate. Completion of the Front End Package for detailed engineering hand-off was completed. The plan for detailed engineering was that it be managed and completed on-site at the Barry Plant by Dow Corning and direct-contract design engineers.

In August 1998 it was decided that a Barry engineering team would complete the detailed design. Many portions of the FEP had been sent to Barry from FE. The design package was being reworked to reduce capital cost.

At Barry in September 1998 the entire Front End Package was received from Midland. Rework for scope changes were targeted to be finished by the end of October. A complete temporary design office was installed for the design engineers. Design team roles and responsibilities were set for the project team. Procurement, purchasing and scheduling roles were established. A 3D CAD package was nominated for design modeling. Discussions with an adjoining (non-Dow Corning) facility regarding joint H_2 supply were terminated. The partner was not interested in a new steam methane reformer.

A detailed report outlining Health & Safety Executive (HSE) concerns about the reactor location was received in September 1998. The main issue was reactor vessel hypothesized catastrophic failure rate and its proximity to the DPR column. A draft revision to the failure rate basis was under review.

Meanwhile, further work was being done to identify a designer for the jet fire wall. Site and project ESD philosophies were refined to bring them in line with regulatory expectations. Approval drawings for the reactor were transmitted to the fabricator.

Barry design package changes were completed in October 1998 per the technology-center cost-cutting meetings in August. A 5-person design team and a team leader moved into the new engineering office. A project kick-off meeting was held to review the project scope.

Manufacturing personnel in Barry questioned three key aspects of the process: likelihood of plugging, conversion of the reactants to usable product, and reliability of the filter. The inability of the Carrollton process to achieve "steady-state" operation while in recycle mode cast doubts about the robustness of the process. The addition of a distillation column to the front end of the process, to replace filtration, was considered.

The Barry design package was put on hold in November 1998; the detailed engineering team was redeployed to work on other projects.

Barry reactor fabrication meanwhile was underway; the cladding was explosion-bonded to the vessel plate steel. Design and drawing reviews were conducted for auxiliary equipment.

Minor work continued as related to the cost estimate, high pressure equipment vendor identification, safety and fire reviews, layouts, revised schedule, project workflow and H_2 supply. No additional procurement was initiated.

A meeting was held with a vendor to review the design of a jet fire wall in December 1998. Various reactor drawings were reviewed. Carrollton maintenance history was reviewed with U.S. personnel.

Limited meetings were held in Barry and minor design activities were completed in January 1999. The project leader took on additional responsibilities in anticipation of the eight month suspension.

The Barry design basis was agreed to during a progress review held 17Feb99. The basis fixed the amount of high-boilers, solids, site rate ramping, and use of other by-products as a solids diluent. NPV calculations were used to evaluate two process options. Flow sheet models and NPV calculations estimated the value difference between filtration and distillation column recovery to be significant. Other efforts included a Methyl DPR trial at an adjacent process's filter in Barry.

Numerous design/scope alternatives were developed for Barry operations in March 1999. Utilization of a process filter was shown to provide the best project Net Present Values. Some process reliability risk was inherent with all the available technology alternatives, and risk was shown to increase with NPV and process yields. The risks and return potential were shared during meetings with stakeholders and again during the March Technology Center meeting. This brought about consensus in favor of the decision to proceed with the filter installation alternative. Business management asked to bring project timing forward. The Barry design team investigated the use of an existing filter in Barry as the hydrogenolysis process filter on a campaign basis .

In April 1999, business management decided to proceed with the Barry filter installation alternative, and asked to bring the project timing forward. Detailed engineering in Barry started back up, having resolved the prior resource issues. A revised schedule for startup timing was forthcoming.

Various Barry mechanical drawings were reviewed during May 1999. The target was to send them to the vendor in July pending the results of the tests in the US. The delivery of key components was scheduled for September 99, but delay was expected as there were still unresolved issues with the corollary Carrollton components.

The Risk Management Portfolio was nearly complete but there were still some project risks that needed to be addressed. The final report was to be completed when those were documented. Once this was done the project risks could be assessed in terms of cost and time impact on the project.

Mechanical tie-ins affecting the adjoining fluid bed reactor (FBR) were being addressed as a priority before the FBR start up. The most critical tie-in was installation of an automated valve on a distillation column for the hydrogenolysis product. The actuated valve was due in late September.

It had become apparent that there was a working filter on-site that was under utilized and had spare capacity that could be used for this process. This was considered as an alternative to a separate, stand alone filter. The hydrogenolysis tower layout reserved space for a future filter.

Use of 3D modeling software began for the reactor assembly. This made the design more efficient and assisted in layout reviews.

The design team was slowly being built up with one full time Mechanical Designer in May, increasing to two in June and also half-time commitment from Instrument Designers.

An order was placed with fire and explosion consultants to carry out Phase II and III of their work for this process.

The reconfigured hot oil and reactor heating system design for Barry proceeded in June 1999. An operating philosophy was developed and reviewed internally. Flow diagrams were drawn. P&ID revisions were underway. Mass and energy balances were started, but still required significant effort. HAZOPs were planned for July. Process data sheets were created for the long lead time instruments. A preliminary equipment list was distributed. Process design resource plans and schedules were created.

Plans for the systematic changeover of the existing on-site filter to dual service were underway in Barry. The change was planned for several phases. Some portions of work were planned for early completion, to improve existing operability and to conduct methyl DPR filtration trials.

Details on the weld overlay of the Barry reactor were being worked out. Overlaid nozzle fabricators were named. Design changes based on the Carrollton experiences were reviewed for application to the Barry design. Barry DC engineers met with the vendor in Germany to review commercial and technical details of the order. The detailed design proceeded for the internal and external attachments and instruments on the reactor.

A Barry project kick-off meeting was held with detailed designers and project sponsors in June 1999. A vendor reviewed high pressure pump alternatives. Meetings were held to review hydrogen supply alternatives and schedule H_2 specification development. Calculations for the development of fire and explosion safety design continued. Plant tie-ins to the FBR were almost complete.

The design of the Barry reactor was going through the final stages of rework in July 1999. Final drawings were due for approval during early August. The Risk Management Portfolio was near completion, but some project risks were identified during the workshop. Mechanical tie-ins affecting the adjoining FBR were addressed as a priority to be completed before FBR start up. The first draft layout of the reactor was reviewed with Safety, Operations and Maintenance. The PMI (Positive Material Identification) for fabricating and installing exotic steels was ready to be issued. This provided the project team with a comprehensive document for identifying, testing, inspecting and storing these materials and preventing mis-allocation with normal carbon steel piping. The design team was slowly being built up with one full time Mechanical Designer for the Reactor Area, one Mechanical Designer for the filter modifications and also two Instrument Designers. The civil design started with the calculation of dynamic and static loads. Fire and Explosion consultants were well into their analysis to determine the most probable causes of an emission from reactor and its impact. The jet fire scenario at the reactor had been modeled in Phase II; the next step was to consider the affects of an explosion resulting from a release of vapor. This information was to be collated with other safety data to demonstrate to the HSE that Dow Corning was considering all safety aspects of the location of the reactor responsibly and professionally. The scope of work for modifying an existing filter for our slurry feeds was developed. The plant modifications were to be funded by this project and a crude estimate for the work based on simple flow diagrams was completed. Tie-ins for this conversion were planned for the September shutdown.

Barry P&IDs were distributed in August 1999, with recent HAZOP action included. Process Flow Diagram schematics were finalized. Mass and energy balances were underway. Equipment data sheets were being revised. Thermal design simulations had begun. Engineering change notes were retroactively written for all the significant changes to the scope. Several details for the weld overlay qualification were reviewed and revised with the fabricators. First revision P&IDs for the filter upgrade were reviewed with manufacturing. HAZOPs were postponed to allow further development of the complete process design.

Consultants completed Barry over-pressure calculations for vapor cloud explosions. The fire wall design proposal was iteratively redesigned to balance jet fire safety with explosion confinement problems. Design criteria for the fire wall were written and were transferred to a fire safety engineer specialist.

Design and supply data were compiled for Barry H_2 supply in August 1999. Suppliers were screened. Three companies planned to bid. Drafts of the scope document were underway.

The Barry Risk Management Portfolio was nearly complete in September 1999. Mechanical tie-ins affecting the FBR were addressed as a priority to be completed before the FBR start up. The process layout, incorporating all the latest process, safety and maintenance requirements, was being developed for the 20% model review in October. A computer 3D model of the plant was being

developed and showed the main items of equipment. The design team augmentation continued. It now included four Process Engineers updating FEP documents for the revised scope of work. There was also one full time Mechanical Designer for the Reactor Area, one Mechanical Designer for the filter modifications and three Instrument Designers.

The Fire And Explosion consultants completed a draft copy of their technical report and the updated Control of Industrial Major Accident Hazards (CIMAH) Safety case for Barry in September 1999.

4.2 Equipment description

4.2.1 Filtered DPR and Monomer Feed Pump

Filtered DPR received from a tank feeds the high pressure DPR pump via a mass flow instrument which controls the speed of the pump, and hence, the DPR flow rate. All other feed material flow rates are set from the DPR flow rate.

Tie-ins to the main supply headers for monomers (from the tank farms) feed separate mass flow instrumentation before combining to provide the high pressure monomer pump with the mixed monomers. The total mixed monomer flow rate setpoint is ratioed from the DPR flow rate, and controls the speed, and thus, throughput of its pump. This, in turn, adjusts the amount of monomer taken from the supply header.

4.2.2 Hydrogen Supply

Hydrogen is supplied from a vendor-provided bottle rack, which is replenished as required from road trailers. A hydrogen feed control station has mass flow instrumentation, relief valves, high and low pressure pre-alarms and high-high and low-low pressure trips. The hydrogen flow rate is controlled by a flow control valve whose flow controller's set point is ratioed from the DPR mass flow rate.

4.2.3 DPR Feed Pre-heater

The DPR feed pre-heater will heat the DPR from ambient temperature using hot oil from the secondary heat transfer loop. DPR heating will be limited in order to reduce its tendency to polymerize. The pre-heater is protected by primary and secondary relief valves on the DPR feed line, and is provided with nitrogen purge and high pressure test points. The DPR is blended with monomers downstream of the pre-heater, prior to entering the reactor.

4.2.4 Monomer Feed Pre-heater

The monomer feed pre-heater will heat the mixed monomers from ambient temperature using hot oil. The mixed monomers are heated in order to reduce polymerization in the reactor by furnishing the heat of reaction, and thus, keeping the temperature differential across the reactor wall as low as possible. The pre-heater is protected by primary and secondary relief valves on the mixed monomers feed line, and is provided with nitrogen purge and high pressure test points. The mixed monomers leave the pre-heater as a super critical fluid, and then are blended with DPR prior to entering the reactor.

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4.2.5 Reactor

The DPR and monomers are reacted with the hydrogen. A higher temperature than normal operation is required to initiate this reaction. The main reaction heat will be contained in the feed monomer.

The reactor oil jacket will also provide additional heat to promote the reaction and to off-set ambient losses.

The DPR and monomers are continuously fed to the bottom of the reactor below the liquid level and intermittently fed to the top of the reactor. Hydrogen is fed to a simple open ended sparger pipe below the liquid level and is mixed with the DPR/mixed monomers. The product will exit from the top of the reactor as a vapor. A sample of the top product will be drawn-off automatically for analysis by chromatographic means. Accumulations of high boilers are blown-down on a timed cycle through the bottom of the reactor. The blow-down procedure includes automatic transfers of the DPR/mixed monomer feed to the top of the vessel for the duration of the blow-down. During this time, the liquid feed is directed via automatic valves to feed pipes on the top of the reactor. The blow-down stream and the vapor top product are combined and fed to a distillation column in an adjacent process.

4.2.6 Hot Oil System

Hot oil, supplied from the main plant heaters, heats a separate hydrogenolysis process "primary" oil loop by means of an oil/oil interchanger. The primary oil loop heats the monomer feed pre-heater and transfers heated oil to a "secondary" loop operating at a lower temperature. The secondary loop heats the DPR feed pre-heater, the reactor, and liquid trace heating of the reactor vapor lines. The main plant and hydrogenolysis process hot oil systems are isolated in order to avoid a shutdown of the main plant process from hot oil contamination caused by chlorosilane leakage from a hydrogenolysis process pre-heater.

The hot oil heating system is comprised of the following.

- An expansion tank, placed at the highest elevation of the oil circuit, which allows initial filling of the system, a volume for the oil to expand and contract as heating and cooling occurs, and a nitrogen blanket.
- Two oil re-circulation loops: a primary loop containing the expansion tank, primary oil re-circulation pump, hot oil / hot oil interchanger and monomer pre-heater; and a secondary loop containing secondary oil re-circulation pump, reactor oil jacket, DPR pre-heater, trace heating circuit, and reactor maintenance cooler.

The two circuits run at different temperatures.

At start-up the secondary will operate to initiate the reaction, having ramped the reactor up-to temperature at a controlled rate. A temperature control valve allows hot oil from the primary circuit to bleed into the secondary loop to maintain the desired operating temperature. The trace heating and the reactor do not have individual temperature control, but the DPR pre-heater's process outlet temperature controls the flow of hot oil through the pre-heater by a valve on the unit's hot oil inlet line.

The primary loop provides process heating for the hydrogenolysis process by obtaining heat from the main plant hot oil heating system via the hot oil / hot oil interchanger. The monomer pre-heater operates on this circuit under temperature control by its process outlet temperature adjusting the flow of hot oil through the pre-heater by a valve on the unit's hot oil inlet line.

When maintenance cooling of the reactor is required, the hot oil supply is shut off to the secondary loop and the secondary loop oil is diverted through an air-cooled exchanger. Maintenance cooling is a manual operation requiring intervention by the plant technicians to operate several manual valves.

4.3 Reactor Wash Out

Operation of the reactor will, over time, cause a build up of solids whose removal will be required on a periodic basis to maintain efficient heat transfer and to prevent pipe and nozzle blockages.

The removal of solids by water or caustic solution boil-outs is as follows.

- Cease normal operation
- Empty reactor to distillation column
- De-pressurize and purge the reactor through with hydrogen
- Nitrogen purge the reactor
- Fill the reactor with Dow Corning siloxane fluid and agitate
- Empty reactor to distillation column
- Connect reactor to portable scrubber, fill with water and heat to boiling
- Cool and dump reactor contents to a skip (portable container)
- Visually inspect the reactor, water blast if necessary
- Purge reactor with nitrogen to ensure complete removal of oxygen
- Dry the reactor by flushing with chlorosilane monomer
- Empty monomer to distillation column
- Purge completely with nitrogen
- Disconnect the portable scrubber
- Pressure test reactor with helium in steps, conducting leak tests at each step

The washing of the hydrogenolysis reactor will utilize existing washout equipment designed for an adjacent reactor, as far as is practical. This procedure is still under development and optimization by Carrollton Manufacturing and Process Engineering.

4.4 Computer Simulations and Results

The stream summary output from a computer process simulator is the basis for the PFD mass and energy balances. The model has been reviewed and validated by existing knowledge of FBR recovery operation's and expected hydrogenolysis performance. The basis and block results for the model are included in a restricted Dow Corning TIS Report [10].

4.5 Materials of Construction

Dow Corning Barry has worked with a number of different suppliers and consultants in an effort to find the appropriate materials of construction for this process.

- Alloy plate and welding wire supplier
- Clad plate supplier
- Head former
- Vessel fabricator
- Nozzle subcontractor

This has resulted in specialized weld procedures for the vessel fabricator and nozzle subcontractor. It has also required some specialized metallurgical testing for weld dilution at various depths in the weld-overlaid portions of the vessel. Special fabrication requirements are demanded in the forming of the shell, heads and post-weld heat treatment of the vessel to prevent heat sensitization of the alloy, which could compromise its corrosion resistance. Various standard tests will be applied to verify the quality of the alloy after different manufacturing steps in the vessel fabrication.

4.6 Design Operational Objectives in the Heating Oil and Feed Preheater Systems

4.6.1 Temperature Differential

The temperature differential across vessel walls will be minimized where polymerization can occur. High temperature differential causes polymerization and solids formation. Polymerization causes corrosion and pitting either indirectly due to aqueous cleaning, or directly through an unknown corrosion mechanism. Polymerization is expected to occur in the reactor and DPR preheater.

4.6.2 Pre-heating Feeds

The heat of reaction will be input to the system through the stable chlorosilane monomers to prevent fouling of the reactor and DPR preheater. The monomers will be heated higher than the normal reactor temperature. This heat will be transferred to the DPR and hydrogen through mixing in the reactor.

Hydrogen will not be preheated due to low mass flow rate (and therefore low enthalpy). It will be fed to the reactor at ambient temperature.

4.6.3 Steady-State Operation

Independent temperature set points for the various heat exchange equipment are required during steady state operation.

It is highly desirable to have no steady state heating load on the reactor jacket. The reactor wall temperature will be maintained via thermal insulation and minimal hot oil flow.

The DPR will be preheated in a preheater with oil, not steam.

The chlorosilane monomer will be heated separately from the DPR. The monomer will be heated above the reactor temperature. The temperature will be set based on the heat of reaction requirements so as to minimize energy input to the reactor jacket. The maximum achievable chlorosilane monomer temperature is limited by the supply oil temperature. This will be a new preheater.

If the enthalpy input to the reactor from the monomer is not sufficient to maintain the reactor temperature, some steady state heating of the reactor jacket will be required. (This is not expected to be the design case for the reactor; therefore, it is not expected to add any significant cost to the project.)

DPR and monomer will not be mixed prior to preheat.

4.6.4 Feed Supply

A new high pressure feed pump will be required to pump up the monomer separately from the DPR. A single machine, high pressure, multiple head pump is also feasible and will be evaluated as an alternative to separate pumps. The selection of the single/dual pumps will consider the following issues: complexity, reliability, cost, instrumentation requirements (stroke adjustment, variable speed drive, etc.) and flexibility.

Additional instrumentation and control equipment will be needed for measuring the flow rates and temperatures of the various separated feed streams.

The monomer/DPR feed ratio will be increased for design purposes to increase dilution effects and minimize solids formation in the reactor. The design feed mixture for 2000 until 2002 is different than the design feed mixture for 2002 onwards.

Future tie-in flanges will be provided for two other monomers.

4.6.5 Transient Conditions

The reactor heating loop must be designed to cope with the following:

Non-steady state heat-up from cold conditions to reaction initiation should be achieved within 12 hours. Due to the high mass of the empty reactor, this will probably be the design case for the reactor heating loop. If this duty drives up system costs excessively, the heating time might be reviewed and relaxed somewhat for cost savings. The reactor initiation temperature is higher than the steady state operating temperature.

Non-steady state cool-down of the reactor will be accomplished via manual change over to cooling through a maintenance cooler already installed in an adjacent process. The cooling time is expected to be approximately 12 hours. Cooling calculations are not required. If the cooler does not have sufficient cooling capacity, a future modification will be made to the system outside the scope of the original project.

The maximum heat up and cool down rate of the reactor must avoid thermal shock of the vessel. The initial heating must not exceed this rate. The maintenance cooling will allow input of hot oil to the reactor loop to temper the cooling if required.

4.6.6 Safety

Safety isolation is required between the hydrogenolysis process oil and the main plant oil supply due to the probability of pitting corrosion, which leads to contamination of the high pressure process fluids with the oil supply. Double tube "safety" heat exchangers have been discussed, but will not be used due to their novelty. Safety isolation requires inclusion of the following equipment which was previously deleted from the scope of the project:

- oil expansion tank
- oil pump
- oil/oil interchanger

4.6.7 Hot oil supply

One new pump will provide fluid flow for and intermediate oil loop. It will provide:

- oil for reactor during reaction initiation
- oil for steady state operation (minimal thermal load, minimal temperature gradient)
- oil through cooler for maintenance
- continuous flow through oil tracer tubes on reactor product pipe to prevent plugging with "condensed" metal chlorides
- oil for DPR preheater during normal operation

5. ENERGY AND WASTE BENEFITS

5.1 Current vs. Proposed Technology Calculation

DPR is currently quenched with a lime slurry that yields a siloxane gel product and lime salts. No chloride ion is recovered by this process. The proposed technology, when fully implemented, will recover more than 80% of the DPR as usable chlorosilanes. These chlorosilanes will then be further processed and the chloride ion recycled. Upon commercialization, the proposed technology will reduce landfill waste by more than 80% and reduce the amount of raw metallurgical grade silicon and chloride ions needed to produce a specified amount of methyl silicones.

5.2 Market Penetration

Dow Corning conservatively estimates that the methyl silicone market will expand 7% per year through the year 2010. The global growth rate from 1978 to 1992 was 9% per year, and SRI International puts the annual growth rate at 7% per year from 1991 through 1994-95 [11]. The current global production of dimethyldichlorosilane is approximately 2.7 billion pounds per year. From the above 7% expansion, the projected dimethyldichlorosilane production will be 6.1 billion pounds per year in 2010. Silicon makes up 21.7 weight percent of dimethyldichlorosilane. Therefore, the current silicone industry demand for silicon is 586 million pounds plus the inefficiencies caused from the byproduct formation of DPR.

DPR constitutes about five weight percent of the Direct Process output - about 135 million pounds per year in today's market (305 million pounds per year in 2010). DPR averages about two silicon atoms per molecule, and has an average molecular weight of 220. Recovering eighty percent of the DPR as useful chlorosilanes saves about 27.5 million pounds of silicon per year. By the year 2010, this savings would grow to 62.1 million pounds per year.

Without implementation of this technology, the current landfill usage will grow at the same rate, as will the demand for make-up chloride ions. Dow Corning is willing to license this technology to other methyl silicone manufacturers.

5.3 Energy and Waste Savings

The Direct Process is not 100% efficient. As much as 5% more silicon is required due to the process inefficiencies. As shown in Table 7, silicon is smelted from quartz in silicon furnaces that use large amounts of energy: 109,322 Btu/lb Si. The proposed process for recovering valuable chlorosilanes from the waste uses relatively little energy: 7,857 Btu/lb Si. Hence, when compared to silicon furnaces, the energy savings is large and silicon efficiency gets closer to unity. In today's market, global implementation of this technology would save $2.8(10)^{12}$ Btu/yr.

Table 7. Energy Savings

A	B	C	D = B - C	E	F = D x E
Description	Current Technology (BTUs/lb Si)	Proposed Technology (BTUs/lb Si)	Energy savings per unit, current less proposed (Btu/lb Si)	Pounds of Si Saved per year in 2010	Energy savings in Year 2010 (10^{12} BTUs/yr)
SiO2	179		179	62,100,000	0.011
Coke	3,792		3,792	62,100,000	0.235
Coal	13,741		13,741	62,100,000	0.853
Electricity (@ 10,500 BTUs/kWh)	69,300	7,857	61,443	62,100,000	3.816
Dry wood chip	13,031		13,031	62,100,000	0.809
Electrode	9,280		9,280	62,100,000	0.576
Total	109,322	7,857	101,466	62,100,000	6.301

5.4 Waste Reduction

The DPR is currently quenched with a lime slurry and landfilled as silica-like product. The hydrolyzed DPR has a molecular weight average of about 160. Approximately 1.5 pounds of calcium chloride salt is produced per pound of DPR hydrolyzed. The proposed technology would reduce the landfilled amount by the efficiency of the process, which is expected to be about eighty percent.

Table 8. Waste Reduction

A	B	C	D = B - C	E	F = D x E
Description	Current Technology (Tons/ton DPR)	Proposed Technology (Tons/ton DPR)	Waste Reduction per unit, current less proposed (Tons/ton DPR)	DPR Recycled in 2010 (10^6 Tons)	Waste Reduction in Year 2010 (10^6 tons/year)
Quenched DPR to landfill	0.73	0.20	0.53	0.15	0.081
CaCl2	1.50	0.22	1.28	0.15	0.195
Total	2.23	0.42	1.81	0.15	0.276

6. BUSINESS

6.1 Economic Attractiveness

Cost analysis of an existing Direct Process train shows that metallurgical grade silicon contributes the greatest share toward the variable cost of basic chlorosilane intermediates. High energy costs associated with the production of silicon metal is the major manufacturing cost. Another significant contributor to variable cost is the loss of chloride due to process inefficiencies, i.e., chloride loss as salt in the lime quench of DPR. There is also the cost to landfill the solids from the quench. Reduction or avoidance of these costs is the prime economic driver.

6.2 Policy/Regulatory

Future chlorine emissions, even in the form of inorganic salts, seem likely to be regulated more severely than they are now. Landfill of even non-hazardous waste (quenched DPR is a non-hazardous waste) is also likely to become regulated in the near future.

6.3 Industrial Competitiveness

All domestic and international silicon 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 potential for escalating environmental regulation. Without the novel waste conversion technology supported by this agreement, competing producers will be at a cost disadvantage in manufacturing methyl silicones.

6.4 Employment Impact

The construction and production of a commercial plant utilizing this novel waste conversion technology will have beneficial employment effects. There are four domestic producers of chlorosilane intermediates. There would be capital spending of approximately $20 million for each commercial process. Upon completion of the process, each commercial unit would require a staff of approximately seven permanent positions.

6.5 Commercialization plans

Dow Corning expects the successful completion of the proposed technology will be readily adopted by the industry under a licensing agreement with Dow Corning. Basic chlorosilanes are manufactured at four sites in the United States. Dow Corning expects all of these U.S. producers to license this technology.

6.6 Foreign Trade

About forty percent of all silicones are manufactured in the United States. Implementing this technology by U.S. manufacturers will give them a lower manufacturing cost 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 market share of the silicone market.

7. PROJECT MANAGMENT

7.1 Research, Engineering and Start-up Plan

Current Activities, FY 1999

- Pilot Plant II Stretch design, procurement and construction (Phase I)
- Pilot Plant II Data analysis
- Full-Scale plant detailed design
- Full-Scale plant procurement
- Full-Scale plant construction (initial)
- Project management and reporting

Planned Activities, FY 2000

- Pilot Plant II Stretch procurement and construction (Phases II & III)
- Full-Scale plant construction (completion)
- Full-Scale plant start-up
- Data Analysis
- Project management and reporting

Planned Activities, FY 2001

- Full-Scale plant commissioning and hand-off to manufacturing
    - ⇒ Investigate reaction conditions
    - ⇒ Investigate feed preparations and compositions
    - ⇒ Conduct capacity test
    - ⇒ Commission plant for use completely by manufacturing unit
- Full-Scale plant data analysis
- Project management and reporting

7.2 Discussion

The plan presented in section 7.1 shows a logical progression from activities at an intermediate level - Pilot Plant II - to activities at Full Scale. These activities overlap, and are consistent with our philosophy to rapidly implement successful, new technology so as to gain competitive advantage. The plan, however, reveals significant delay, when compared to the plans presented in previous technical annual reports [13]. Reasons for these delays are numerous.

- Dow Corning Corporation is in Chapter 11 bankruptcy status; this began in 1995. Cash flow has been severely restricted during Chapter 11, even for projects like DPR Hydrogenolysis that have great benefit.
- In 1996, a decision was made to not scale up directly from Pilot Plant to Full Scale, but rather build and operate Pilot Plant II as an intermediate step. The desired outcome of the decision was to lower our overall risk due to technical uncertainties.

- Pilot Plant II operational difficulties delayed the confirmation of this technology as feasible. These difficulties included poor valve performance, rotating equipment malfunctions, reactor steel corrosion, and the handling of solid byproducts formed in the reactor.

Table 9. Milestone complete dates

Milestone	Date of Estimate	Planned	Actual Completion
Pilot Plant			
Detailed design	10/13/93	1/1/94	12/31/94
Procurement and Construction	10/13/93	08/31/94	12/31/94
Start-up	02/28/95	4/30/95	05/31/95
Operation	02/28/95	10/31/95	03/31/96
Data Analysis	02/28/95	10/31/95	06/30/96
Economic analysis and commercialization plan	02/28/95	3/31/96	12/31/95
Pilot Plant II			
Technology package	4/10/96	03/11/96	01/31/96
Project package	4/10/96	02/15/96	02/28/96
Detailed engg: Design/procure	4/10/96	11/30/96	01/31/97
Construction	4/10/96	12/13/96	03/31/98
Safety training: pre-start-up	4/10/96	01/15/97	03/31/97
Process start-up	4/10/96	02/28/97	02/28/98
Process optimization	4/10/96	05/16/97	11/30/98
Econ analysis and commercial plan	4/10/96	06/30/97	01/31/98
Project management and reporting	4/10/96	06/30/97	12/30/98
End of Phase IIIA	4/10/96	06/30/97	11/30/98
Full scale			
Preliminary engineering	08/18/99	09/20/99	01/31/98
Cost estimate	08/18/99	11/01/99	08/31/98
Permitting	04/10/96	08/31/97	03/31/98
Detailed design	08/18/99	11/15/99	
Construction/procurement	08/18/99	08/07/00	
Start-up	08/18/99	08/31/00	
Data analysis and performance update	08/18/99	09/30/00	
Project management and reporting	08/18/99	09/30/00	
End of Phase IIIB	08/18/99	09/30/00	
Full scale - demonstrate reaction conditions	08/18/99	11/30/00	
Feed preparation requirements	08/18/99	01/31/01	
Feed composition	08/18/99	03/31/01	
Capacity testing	08/18/99	05/31/01	
Data analysis and performance update	08/18/99	05/31/01	
Commissioning test: hand off to manufacturing	08/18/99	05/31/01	
Project management and reporting	08/18/99	09/30/01	
End of Phase IV	08/18/99	09/30/01	

7.3 Industry/Department of Energy Cooperation

Table 10 shows the sources of funding for this project. The data in this table are available in Dow Corning's Continuation Application for this project [14]. The Department of Energy is the only external funding source for this project. DOE's contribution to this project is about 6.6% of the total project cost, and was weighted towards the front-end, high-risk portion of the project.

Table 10. Industrial Participation

Partner	Cost Sharing, Federally Allocated Resources	Cost Sharing, Non-Federally Allocated Resources	Total
DOE	$1,716,701		$1,716,701
Dow Corning	$24,124,533		$24,124,533
Total	$25,841,234		$25,841,234

8. SUMMARY

The Pilot Plant II hydrogenolysis reactor has demonstrated filtered DPR conversion between 59% and 89%. Valuable monomer production has been greater than expected. Significant obstacles were overcome during its operation from May 1998 through September 1999, such as mechanical malfunctions, high-pressure feed-pump failure, and reactor corrosion. Significant improvements compared to the previous year's operation were made in the areas of product value and overall reliability. A plan is being executed to increase the capacity of Pilot Plant II four-fold by the end of 2000.

Design efforts for the Full-Scale unit in Barry, Wales are near completion and construction has begun in earnest. Start-up targeted to be complete by first quarter of 2001.

9. EXPERIMENTAL

9.1 Analytical Methods Used for Feed and Product Samples

9.1.1 Laboratory gas chromatograph

The determination of compositions for the various streams in the Pilot Plant II can be achieved using gas chromatography (GC). These analyses incorporate an octane internal standard which is added to each sample analyzed. In general, results are very similar to those obtained from previous runs in the laboratory and pilot plant in terms of the amount of non-elutable species which were found to exist as indicated by the internal standard. It is common for 10 to 15% non-elutable species to be found present in feed samples, which were, in turn, assumed to be high boilers. Bottoms product samples are often less than 50% elutable.

Based on the predictability of non-elutable fractions in the feed and product samples and the greater need to have timely identification of low boilers in product samples, it was decided that a dedicated GC was to be installed at Pilot Plant II as part of the capital project. The on-line analyzer is used for overhead vapor product samples only. Such an analyzer is readily monitored by operators and engineers, contributing to their ability to make good decisions on a daily basis.

9.1.2 Pilot Plant II gas chromatograph

The Pilot Plant II GC is equipped with a column and helium carrier gas.

The capability for on-line, automatic sampling of feed and product streams exist. All runs have utilized this capability. A method for automatic calculation of stream compositions is programmed into the Pilot Plant analyzer PC. All samples analyzed on the Pilot Plant II GC are analyzed without an internal standard.

The Pilot Plant II GC is calibrated periodically. In particular, it is calibrated on a monthly basis in accordance with quality procedures written to comply with ISO 9001 standards. Calibrations are performed by injecting a sample from a refrigerated vial containing a previously prepared standard solution of methyl chlorosilanes. The results of each calibration run are compared to weight percent ranges for three key components as determined from historical data for the standard.

9.2 Other Analytical Methods

Other testing was performed by research analytical (elemental analysis), Carrollton plant QA (% solids, $\%O_2$ in reactor head space during pre-startup inerting), Midland analytical (CHN analysis, solids NMR), or outside personnel (various safety tests) as needed, according to standard methods. The use of data from these various tests is much more limited to specific sections and discussion of specific topics related to Pilot Plant II operation.

10. FUTURE WORK

Future work for Pilot Plant II will concentrate on increasing its capacity four-fold by the end of 2000, as discussed in detail in Section 3.

The effects of total DPR recycle will continue to be investigated. For the Pilot Plant II system, this means only feeding the adjoining FBR's DPR to Pilot Plant II, and never pumping the adjoining FBR's DPR to any other destination. The intent is to complete a metal chloride and high boiler mass balance, and determine the effect on filter element life and reactor conversion. The results of this trial will confirm the full-scale process's design decision to install a filter upstream of the reactor, instead of a flash still after the reactor to purge the high boilers to a by-product chlorosilane hydrolysis process.

Corrosion testing will continue in the Pilot Plant II reactor. The corrosion coupons inside the Pilot Plant II reactor will be analyzed. This will involve removal of the reactor head. The corrosion coupons in the reactor will help verify the choice of materials for Pilot Plant II Stretch Project and the Barry unit. Non-destructive testing of the Pilot Plant II reactor and piping will also be performed.

Evaluating alternative ball valves to replace the existing valves at Pilot Plant II will continue. This effort began in mid-1997 during the original start-up of Pilot Plant II, and has yet to be resolved. Valve maintenance and replacement at Pilot Plant II continues to incur unacceptably high expense. At least four different valves have been installed for testing. Final vendor selection will be determined by degree of shut-off, cost, delivery time, operability, stem leaks, and body leaks.

Future work at the Barry site is discussed in detail in section 4.

11. REFERENCES

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