OCIM August 2024 Fatal Accident Analysis

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Summary
There is no known organization that promotes routine sharing of process safety information across the global solar-grade polycrystalline silicon industry. This is a major shortcoming of this industry. Shared experiences (good and bad) have the real chance to improve the overall process safety of the entire industry. A major accident by one producer, such as the OCIM August 2024 or Xinjiang GCL July 2020 incidents, can give the entire industry a negative reputation. This document has been prepared to informally provide important process safety analysis and information with the intent to help prevent future similar accidents.

OCIM experienced a major process safety upset on one of their hydrochlorination (HC) ($Si + 2H_2 + 3SiCl_4 = 4HSiCl_3$) TCS (trichlorosilane; $HSiCl_3$) synthesis units on 14-August-2024 at the Bintulu, Sarawak, Malaysia site. Ten people were injured and two of these died in the weeks following the accident. OCIM has not released any information about the accident as of mid-November 2024. The accident resulted in what is clearly a de-inventory / de-pressure of a HC synthesis reactor and associated process piping given the massive cloud of hydrogen chloride (HCl), steam and fine solids that was generated. The accident appears to have occurred with one of the four original Tokuyama Phase-2 HC units and specifically in the bottom area of one HC reactor. The site was originally built by Tokuyama. Tokuyama had significant problems with commissioning and startup and sold the site to OCI (South Korea).

This document was prepared with the intent of analyzing the OCIM accident using available visual accident information (photographs and video) combined with the first-hand author experience with HC unit design, operation and maintenance. While some unconfirmed information about the accident cause(s) have been reported, the analysis presented in this document avoids the use of these sources. The resulting analysis is an experienced-based list and detailed discussion of potential failure areas located in the bottom HC reactor area.

An assumption is made that the main gas feed pipe was constructed of Incoloy 800H (UNS N08810). Use of Incoloy 800H is well known by all industrial HC operators and is recognized as the only ***proven*** material of construction for use in specific areas of the HC unit. Some different materials are known to have been recently used by some producers, but there is no long-term safe history of these materials. If OCIM were to have used something other than Incoloy 800H in the area of the fatal accident, this would then become a strong root cause suspect.

A summary of potential failure modes of the OCIM HC reactor is provided in the following table. The five identified failure modes represent possible causes of the OCIM August 2024 accident.

Failure Location	**Potential Failure Causes**			
1) Main gas feed pipe	Internal corrosion	Internal erosion	Failure to follow best practices for Incoloy 800H piping fabrication	Excess thermal pipe stress
2) FBR vessel wall @ grid attachment	Wrong grid attachment mechanical design			
3) Anhydrous HCl co-feed pipe	Internal corrosion	Internal erosion	Failure to follow best practices for Incoloy 800H piping fabrication	Excess thermal pipe stress
4) FBR vessel welds	Failure to follow best practices for Incoloy 800H vessel fabrication			
5) FBR vessel nozzles	Failure to follow best practices for Incoloy 800H vessel fabrication	Internal corrosion	Internal erosion	

<u>Failure Hypotheses:</u>

1) OCIM could have failed to implement and execute routine mechanical integrity checks of process lines including visual internal inspections of the main gas feed pipe. Routine internal corrosion was not recognized.

2) A change could have been made to the ground MGS particle size distribution (PSD) that resulted in an elevated amount of MGS ‘sifting’ through the grid holes and into the area under the grid and into the main gas feed pipe. Localized erosion of the main gas feed pipe was not recognized.

3) OCIM could have poor return to service procedures with regards to ensuring process piping, such as the main gas feed pipe, is properly cleaned of internal solids and properly dried before returning to service. Failure to dry and clean can result in accelerated HCl-related corrosion.

Recommendations

Regardless of the validity of the information received about the OCIM fatal accident and the analysis presented in this document, the following recommendations are made. These recommendations must be carefully evaluated by subject matter experts (such as those with Incoloy 800H piping design experience) prior to implementation.

Any industrial operator of a hydrochlorination (HC) ($Si + 2H_2 + 3SiCl_4 = 4HSiCl_3$) crude TCS synthesis unit, whether for TCS-based polysilicon production, silane (SiH_4) based polysilicon production or merchant silane gas production is strongly advised to heed this recommendations as soon as possible. This statement applies to both long-term legacy HC operators, newer entrants (China, Malaysia, South Korea) and Indian projects that are currently in the design / engineering phase.

1) Any current operator of an industrial HC TCS synthesis unit, regardless of experience or plant status (from early design phase through multi-year industrial operation), is recommended to consider conducting an independent review of all aspects of process safety with regards to HC unit process design, operations and maintenance strategy.

2) Examine the following questions: Has the specific site adopted the USA OSHA 1910-119 standards with regards to plant design, operation and maintenance? If not, why? Is the site using a similar system instead?

3) Review the site mechanical integrity inspection program (routine external pipe thickness measurements, for example, and non-routine visual internal inspections) and determine if the current program would identify localized erosion / corrosion of the main HC FBR gas feed pipe prior to catastrophic failure.

4) Review the site standard operating procedures including “return to service.” Do these procedures address visual inspections of process equipment and piping to ensure that hygroscopic solids (easily “taking up water”) have been removed prior to restart?

5) Check the following item: Does the site have an adequate management of change (MOC) program that would identify a process change, such as new particle size distribution (PSD) of ground metallurgical grade silicon (MGS), as placing a risk to safe operations?

6) Review current quality control plan for purchased ground MGS or MGS that is ground on-site to ensure that the current ground MGS powder PSD specification is always achieved.

7) Any industrial HC operator that has not implemented a formal mechanical integrity checking program nor has routinely used a mechanical integrity program (both routine external measurements and visual internal inspections during all planned maintenance outages) is recommended to carefully inspect all main gas feed piping between final superheaters and the inlet to the HC FBR as soon as possible. If the history of the piping

is not known in terms of original fabrication and designs to accommodate thermal stresses, the best action would be to replace all main gas feed piping.

8) A review of known HC FBR Piping & Instrumentation Diagrams (P&ID's) shows that none of these designs include emergency isolation valves on the main gas feed line and other gas feed lines to the FBR vessel. Why are these valves not included? Known industrial reactors methylchlorosilane synthesis and direct chlorination TCS synthesis have such valves. These valves are designed to prevent exactly what happened at OCIM should a feed line fail – catastrophic de-inventory of the HC fluid bed reactor (FBR).

9) New corrosion studies are recommended to be conducted for applicable materials of construction such as Incoloy 800H (UNS N08810) for the following systems:

   a. **System-1**: H_2 – STC

   b. **System-2**: H_2 – STC – HCl

   c. **System-3**: H_2 – STC – HCl – Metallurgical grade silicon

   Results of these studies must be published in the public domain, preferably in a peer-reviewed journal. The technical procedures followed by Union Carbide in the only public domain corrosion study that includes Incoloy 800H (UNS N08810) for the specific system H_2 – STC – Metallurgical grade silicon should be followed for new corrosion studies.

Report Format

The overall goal / purpose of this report is to reduce this risk of employees working in polysilicon plants to death or serious injury. There have been several significant accidents within the global polysilicon industry since 2014. Overall industry risk remains very high based on the massive increase in global polysilicon capacity.

The industry does not have noticeable plan or program to address process safety for a wide range of reasons. As a result, detailed, fact-based combined with experience-based identification of possible problem areas analysis, generated by independent people working in the industry are necessary to improve the level of safety awareness. This report provides one example of increasing awareness of polysilicon plant operators about potential chronic process safety problems.

This lofty goal is to be achieved by providing operators of polysilicon plants (trichlorosilane [TCS; $HSiCl_3$] or silane [SiH_4] based) where TCS is synthesized by the hydrochlorination (HC) ($Si + 2H_2 + 3SiCl_4 = 4HSiCl_3$; also called hydrogenation [Union Carbide / ASiMI / REC Silicon]; cold hydrogenation [China]) with analysis of a fatal accident that occurred at the OCIM polysilicon plant on 14-August-2024.

OCI Korea nor OCI Malaysia (OCIM) have not released any information about the accident. There are some unconfirmed reports from local non-OCIM sources about what happened. These unconfirmed reports are not included in this report. Detailed, experienced-based analysis of the accident photos and video that were posted on social media combined with Google Earth image analysis have enabled the author to identify the general location of the failure resulting in the accident. Based on this experienced-based analysis, a list of probable failure causes will be developed and discussed.

A. Introduction to the OCIM August 2024 Fatal Accident

Provide a brief summary and pictures of the OCIM accident based on media reports.

B. Provide Relevant Background on the Industrial Hydrochlorination Process

Analysis of the accident requires the reader to have some knowledge of industrial HC process unit design and operation. This section provides some basic technical information that provides important context once the accident analysis sections are presented. There is no way for the information provided in this section to be all encompassing. The reader is encouraged to find experienced information sources to provide additional information if required.

1) OCIM Introduction

2) Fluid bed reactor introduction

3) Hydrochlorination Process Unit Safety Benchmark

4) Hydrochlorination Unit Materials of Construction

5) Make-up Chlorine Sources

6) Ground Metallurgical grade silicon Particle size distribution

C. Location of Likely OCIM Equipment Failure

Provide details of how analysis of photos and video from the OCIM August 2024 accident were used to determine the likely location of the equipment failure.

D. Identify Specific Equipment that Failed, List and Analyze Possible Causes

This section provides an experienced-based list of exactly what equipment failed, the possible causes of the failure and analysis of the possible causes.

E. Appendix A: Chronological Details of the Malaysia site development

The Bintulu, Sarawak, Malaysia site has a complex history. Relevant information about the Tokuyama era, the Tokuyama technology provider, the OCI era and some Google Earth image analysis are presented.

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There is No Relationship between report Author and OCI

There is no current nor has there been a historical relationship between the author of this report and any part of OCI: OCI Korea, OCI Malaysia, OCI Corporate and others. The author has never been a direct employee of any part of OCI nor has the author worked as a direct consultant with any part of OCI. There are no past or current non-disclosure agreements in place between the author and any part of OCI. This report was prepared with zero input from OCI.

OCIM Site Safety Culture

The OCIM site has an extremely serious problem with "safety culture". First-hand experience working in the global polysilicon and silicone industries since 1989 shows that the overall "safety culture" of these sites is driven by a top-down approach from upper management (CEO / owner level). Upper management must demand that site operations and maintenance be conducted at the highest level of overall safety. Safety includes safety of all site employees, safety of the surrounding communities and safety of the environment. Information found in the public domain shows that the OCIM site has had chronic problems with safety almost since OCIM restarted the site in late 2017 after acquiring from Tokuyama. By the end of 2024, there have been four documented worker fatalities.

There was a serious process safety incident on 11-October-2019 that appears to have occurred in the bottom area of a Hydrochlorination fluid bed reactor and generated a large cloud of HCl. A local media report (see: https://www.thestar.com.my/news/nation/2019/10/12/swift-action-by-firemen-averts-explosion-at-s039wak-silicon-plant?fbclid=IwAR0JlIUocSaWr3VdoK_I2h5b1eZRaP246bbQEaIlc_WuSrC1999EuiiCd5U) shows the OCIM "fire brigade" spraying water on a process vessel (likely a hydrochlorination fluid bed reactor). Amazingly, the members of the "fire brigade" are not wearing any normal protective gear that would be standard issue such as fire turnout gear and SCBA systems (SCBA = self-contained breathing apparatus). The photograph provides yet additional incriminating evidence that the OCIM site has a serious problem with "safety culture". There were no reports of injuries or fatalities.

A recently published report from Germany (see: https://www.fian.de/aktuelles/siliziumproduktion-in-malaysia-gefahr-fuer-mensch-und-umwelt-aus-foodfirst-04-2024/) provides new information about the chronic problems at OCIM. This report mentions a hydrogen explosion at the OCIM site that killed two workers on 9-May-2022. The German report also discusses chronic discharge of waste streams from the OCIM site that is harming local food supplies.

The purpose of this report is to analyze the fatal accident that occurred on 14-August-2024 at OCIM. Two workers died of injuries suffered in the weeks following the accident; eight additional workers were injured. Immediately following the August 2024 fatal accident, there were reports in local media of another serious accident that happened in May 2024 but details were not provided.

Limited public domain information clearly shows that there is an extremely serious problem with the OCIM site in terms of process safety. It is well beyond the scope of this report to determine the root causes of the chronic serious safety issues at OCIM. This matter requires immediate attention or, sadly, the trend of process safety incidents resulting in serious injury, death and off-site impact will continue. OCI top management is urged to admit to the serious problems that exist at OCIM and seek the necessary help required to stop this trend.

OCIM August 2024 Fatal Hydrochlorination Unit Accident Overview
The polysilicon plant operated by OCI in Bintulu, Sarawak, Malaysia (OCIM) experienced a significant process safety incident on 14-August-2024. The incident resulted in immediate injury of 10 workers with four of the 10 requiring admission to the local hospital intensive care unit (ICU). Two of the 10 workers died: one on 29-August-2024 and one on 8-September-2024. Unknown is whether the two workers who died were amongst the four admitted to the ICU.

A local Bintulu media source reported on the day of the accident that the fire broke out at the "*bottom reactor tank*" of the OCIM plant. See: https://www.theborneopost.com/2024/08/14/plant-fire-at-samalaju-industrial-park-leaves-10-injured/). General media reports about chemical plant accidents are typically error-prone. This report's use of "*bottom reactor tank*" could also be confusing based on translation from Malay (or other local language) to English.

Two screen shots from a video posted on-line shows the massive cloud. The cloud is likely a combination of hydrogen chloride (HCl) (from reaction of chlorosilanes with moisture in the air and maybe fire-fighting water), steam (from burning H_2) and fine solids.

OCIM has offered no official press release about the accident. The author of this document has contacted the OCIM press contact and the overall OCI Corporate (South Korea) investor relations (IR) contact two times asking for additional information. OCI did not reply. The same OCI Corporate IR immediately responded to the author in 2023 when an inquiry was made about forced labor and Xinjiang Province, China. Local Sarawak media reported at least one other accident earlier in 2024.

Detailed experienced-based analysis of the photos and video of the OCIM August 2024 fatal accident to be presented in a later section of this document, clearly identify that the OCIM accident occurred within one of the Hydrochlorination (HC) ($Si + 2H_2 + 3SiCl_4 = 4HSiCl_3$) TCS synthesis process units. This statement is made with a very high level of confidence based on the visual accident evidence and review of Google Earth images of the OCIM site. Discussion in the remainder of this document will be based on the accident occurring within an HC unit. Details about specific accident location, what may have failed and causes of the failure will be developed in the remainder of this document.

Figure 1: OCIM 14-August-2024 accident. The three units with top cubic enclosures are three hydrochlorination process units. These cubic enclosures likely contain the ground metallurgical grade silicon feed systems.

Figure 2: OCIM 14-August-2024 accident. This photo provides a perspective of the enormous size of the cloud. The only known polysilicon accident of similar magnitude is the July 2020 Xinjiang GCL incident.

OCIM August 2024 Fatal Accident

Identification of Accident Location

The purpose of this section is to identify the location of the OCIM August 2024 fatal accident. The identified location starts with the main process unit followed by the specific area of the identified process unit. Identification will be accomplished by use of published photographs and videos of the August 2024 accident along with Google Earth images of the OCIM site and other published pictures. These images are then combined with 20+ year first-hand knowledge of how industrial polysilicon plants are designed to arrive at a credible accident location.

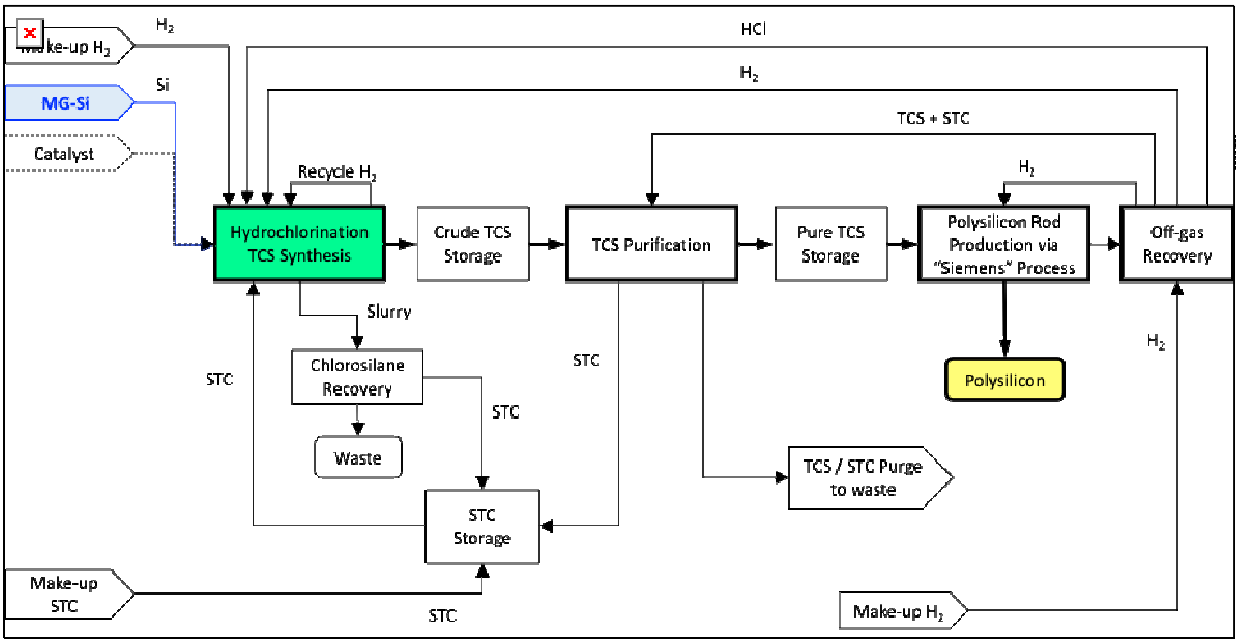
Later sections of this report will list specific equipment (piping and / or vessels) that are present in the identified accident location the failure of which could result in the massive “cloud” that formed immediately following the accident (See Figure 1 and Figure 2). Analysis will then be conducted of the possible failure modes of each separate piece of equipment (piping and / or vessels) identified. The analysis will include examples, where applicable, of known historical industrial process unit failures. The analysis will also discuss the likelihood of such a failure actually being the cause of the OCIM August 2024 fatal accident.

The reader is reminded that all of this analysis is based on 20+ years direct industrial experience of polysilicon plant design and operation and 35+ total years industrial experience with design and operation of industrial silicon-chemistry plants including silicones (organosilicon).

The overall analysis is viewed by the author as important and applicable regardless of the accuracy to identify the actual cause of the OCIM August 2024 fatal accident. All scenarios identified will be valid and should be the topic of any correctly conducted HAZOP (Hazard and Operability Study).

OCIM Introduction
The OCIM polysilicon plant located in Bintulu, Sarawak, Malaysia produces solar-grade polysilicon rods from ultra-pure trichlorosilane (TCS; $HSiCl_3$) by batch chemical vapor deposition. Polysilicon (solar or semiconductor grades) is one of the purest human made materials produced on large global scale. Metallurgical grade silicon (MG-Si) enters that plant at a purity of about 99 weight % silicon. Solar-grade polysilicon product leaves the plant at a purity of about 99.9999999 weight % silicon (9 "nines" or 9N). Figure 3 provides a high level view of the OCIM TCS-based polysilicon process. Each box in Figure 3 represents a major process unit within the overall site.

Figure 3: High level view of TCS-based polysilicon plant where TCS is produced by Hydrochlorination ($Si + 2H_2 + 3SiCl_4 = 4HSiCl_3$). Make-up chlorine is provided by purchased STC. An alternate source of make-up chlorine will be discussed later in this report.



OCIM produces crude TCS with the hydrochlorination (HC) ($Si + 2H_2 + 3SiCl_4 = 4HSiCl_3$) process. The HC process is known as the "hydrogenation process" at REC and commonly called "cold hydrogenation" by Chinese producers.

> *Usage of "hydrogenation" by REC and "cold hydrogenation" by Chinese should not be confused with another "hydrogenation" process where silicon tetrachloride (STC; $SiCl_4$) is reacted with HCl at high temperature to produce TCS ($SiCl_4 + H_2 = HSiCl_3 + HCl$). This hydrogenation process is not used by TCS-based polysilicon producers where HC is the TCS synthesis route. Hemlock Semiconductor and Wacker use this high temperature hydrogenation process; the main TCS synthesis route used by Hemlock and Wacker is direct chlorination (DC) ($Si + 3HCl$ ✍ $HSiCl_3 + H_2$). High Pure Silicon and Tokuyama also use DC as the main TCS synthesis route.*

Crude TCS is purified in a series of distillation columns and, usually, specialized unit operations designed to remove specific impurities such as volatile forms of boron, carbon and phosphorus. Ultra-pure TCS exits the purification section of the plant and is stored in dedicated tanks.

The pure TCS is mixed with pure H_2 and fed to multiple batch operated Siemens CVD reactors where it is converted to polysilicon. These reactors are commonly called “Siemens reactors” as Siemens AG (Germany) was an early developer of the technology. The polysilicon is “grown” in the form of multiple rods that are perhaps 90 – 120 mm diameter and 2 meters tall. The reaction consumes large amounts of electricity (about 40 kW-hr/kg polysilicon). The polysilicon rods are “harvested” at the end of each batch reactor run. One batch reactor run lasts about 72 hours. The harvested rods are transported to a product finishing area where the rods are crushed to lumps and packaged for shipment to customers. The product finishing area is operated as a clean room.

Off-gas from each of the CVD Siemens reactors is collected and piped to the off-gas recovery (OGR) section of the plant. The combined off-gas stream contains unreacted TCS, unreacted H_2, by-product STC, by-product HCl, small amounts of other by-products and some fine silicon dust. The purpose of the OGR unit is to separate this complex stream into the pure components. The pure components (TCS, H_2, STC, HCl) are then recycled to the appropriate process units.

The polysilicon plant also requires unique processes to handle a wide range of dangerous waste streams generated through normal operation. These waste streams include solids, slurry, liquids and gases. The goal of the overall waste handling processes is to recover and recycle, where possible, valuable chlorosilanes (TCS and STC for example) and to safely neutralize the remaining streams before discharge to atmosphere, water or suitable landfills.

With the exception of the batch CVD Siemens polysilicon reactors, the remaining process units are operated continuously. These continuously operated units are normally shutdown once per year for maintenance and inspections. The plant is heavily automated and controlled from a central control room. The automation includes remote monitoring and computer control of process conditions such as temperature, pressure, flow rates and process vessel inventory. An important part of the control system is the overall safety system. State of the art polysilicon plants normally have redundancy built-in to the safety systems.

The OCIM TCS-based polysilicon plant has the same general process design as all operating Chinese TCS-based polysilicon plants. REC Silicon does not produce polysilicon from TCS but, instead, from silane (SiH_4). REC Silicon solar-grade polysilicon is produced via the fluid bed reactor (FBR) process. The FBR process yields granular polysilicon instead of rods. REC Silicon does produce crude TCS via the same process as OCIM. GCL Poly (China) uses the same general process as REC Silicon to produce granular solar-grade polysilicon.

Identify OCIM August 2024 Fatal Accident Process Unit
Analysis of the photographs and video from the OCIM August 2024 accident combined with analysis of Google Earth images of the site and related published site photographs clearly indicates that the accident occurred within one of the Hydrochlorination (HC) ($Si + 2H_2 + 3SiCl_4 = 4HSiCl_3$) trichlorosilane (TCS: $HSiCl_3$) synthesis units. Specifically, the accident originated within the HC reactor process tower. Analysis resulting leading to these statements is provided below.

A. Visual Evidence – Color of the released "Cloud"

The primary visual evidence that indicates the accident occurred in a HC unit is the color of the "cloud" visible in the pictures (See Figure 1 and Figure 2). The dark color of the cloud indicates the presence of "reaction mass" from the HC fluid bed reactor. The "reaction mass" is metallurgical grade silicon (MGS) that is ground to a fine powder. The particle size distribution (PSD) of the ground MGS powder is similar to beach sand. The color of MGS is metallic gray. First-hand experience with observations of "many" large releases of MGS to the atmosphere over the years shows a very distinctive dark "cloud". There are very few locations within a polysilicon plant that can generate such a large dark cloud.
Figure 4 shows a screen grab from a video posted on social media. Note the very dark color of the cloud.

Exposure of chlorosilanes, such as silicon tetrachloride (STC; $SiCl_4$) and trichlorosilane (TCS; $HSiCl_3$), to the atmosphere always results in formation of a large white cloud of hydrogen chloride (HCl) gas. All chlorosilanes react with moisture present in the air to form HCl gas and silicon-oxygen compounds called siloxanes. When the chlorosilane contains hydrogen, such as TCS, not only is HCl and siloxanes formed but also some Hydrogen (H_2) is generated. Depending on the type of fire protection system present in a plant, additional HCl gas can be generated by application of water, by either fixed fire protection of fire apparatus, to "knock-down" the cloud. Details of OCIM fire suppression systems are not known.

Chlorosilanes are present in several of the main process units of a polysilicon plant: HC TCS synthesis, crude TCS storage, TCS purification, Pure TCS storage, CVD reactor off-gas recovery, Chlorosilane recovery and STC storage (these process units are taken from Figure 3). A major accident in one of these areas, OTHER THAN the HC TCS synthesis unit, would result in a large "cloud" but the color of the cloud would be white (similar to a cloud of steam) or off-white. These process units (other than the HC TCS synthesis unit) do not contain ground MGS powder. The color of the cloud from the OCIM August 2024 accident is clearly not white or off-white. This indicates the accident DID NOT occur in those units that do not contain MGS. Figure 5 shows a typical white HCl cloud resulting from just a chlorosilane release. This picture was from a large process safety incident that occurred at Wacker Polysilicon located in Charleston, Tennessee, USA on 7-September-2017.

Figure 4: A screen grab from a video of the OCIM August 2024 fatal accident. Note the very dark color of the "cloud" which is indicative of high concentration of MGS powder. The process structures in this picture are clearly HC units (see discussion later in this section). There is no bulk MGS storage in this area.

Figure 5: Photograph taken during a large chlorosilane release at the Wacker Polysilicon plant located in Charleston, Tennessee, USA on 7-September-2017. The white "cloud" is primarily HCl gas and a good example of a cloud resulting only from chlorosilane release. There were no serious injuries resulting from this accident. The accident was caused by a compressor failure.

The industrial HC process unit also includes large amounts of H_2. H_2 is also present in polysilicon Siemens production unit and the CVD reactor off-gas recovery unit. H_2 spontaneously combusts upon release to the atmosphere to produce water: H_2 + ½ O_2 ✍ H_2O. Some of the water formed from H_2 combustion will react with chlorosilanes to produce HCl gas and some of the water will be released to the atmosphere. Since the released H_2 from the accident is at elevated temperatures, the released water will be as steam. Steam clouds are white. The color of the OCIM August 2024 accident cloud is clearly not white. The only plausible source of a dark material to result in the gray cloud is large amounts of MGS and the only polysilicon unit that has large amounts of MGS that can be easily mixed with chlorosilanes (STC, TCS) and H_2 is the HC TCS synthesis unit.

B. <u>Process Unit Configuration</u>

Almost as important as color of the released cloud is the physical design / configuration of the process units that are clearly visible in the photographs and video as the original source of the cloud. First-hand knowledge of the original source of the HC TCS synthesis units used in the OCIM site provide a clear identification that the accident originated in the HC unit. Appendix A provides some details about the history of the OCIM site.

The main identifying features of the original OCIM HC TCS synthesis units are: 1) the structure (sometimes called the "process tower") is tall. All HC fluid bed reactors are tall, cylindrical vessels that are over 9 meters tall. These vessels are supported by structural steel. Ground MGS powder for the original HC reactor design used on the OCIM site was added to the top of the individual HC reactors.

The MGS feed system is located vertically above the HC reactors and consists of a low-pressure "receiving hopper" (ground MGS is transferred from a large storage vessel to the low-pressure "receiving hopper" located at each HC unit. A high pressure "feed hopper" is located below the "receiving hopper" and above the top of the HC reactor. Ground MGS powder is gravity fed from the receiving hopper to the high pressure "feed hopper". The contents of the "feed hopper" are pressurized to a value higher than the operating pressure of the HC reactor and then the ground MGS powder is transferred into the top of the HC reactor.

Given the overall design of the ground MGS powder feed system (vessels, filters, piping and instrumentation), it is common to enclose this section. The distinctive MGS feed system enclosures are clearly visible in the accident photographs and the origin of the "cloud" is clearly from somewhere within the HC process unit. Figure 6 (same as Figure 1) identifies three HC reactors and the accompanying MGS feed systems are clearly visible. The release, as indicated by the massive "cloud", is clearly originating from one of these units (looks like the one on the right of the picture).

Figure 6: Cropped version of Figure 1 showing the large cloud of HCl and MGS originating at one (of three) HC process units at the OCIM site. There are three HC process units in this picture and each is marked by the distinctive enclosed MGS feed system which is the highest point of each unit. This enclosed MGS feed system located above the HC reactor is a distinctive feature of the specific HC technology used in these units.

Where was the Failure within the HC Process Unit Tower?
The previous section concludes that the OCIM August 2024 fatal accident occurred within one of the Hydrochlorination (HC) ($Si + 2H_2 + 3SiCl_4 = 4HSiCl_3$) trichlorosilane (TCS: $HSiCl_3$) synthesis units. Specifically, the accident originated within the HC reactor process tower. The analysis in this section shows that the accident appears to have originated in the bottom area of the HC reactor process tower. This is critical knowledge as it significantly reduces the potential areas that could have failed.

A. Visual Evidence – Origination of the "Cloud"

Visual evidence is again used in this analysis. The best visual evidence is a video of the accident that was posted on social media. Beginning at the 11 second mark of the 23 second movie, a dark cloud is viewed forcefully flowing in a horizontal movement from an area close to the ground. A screen shot of the video at the 11 second mark is shown in Figure 7.

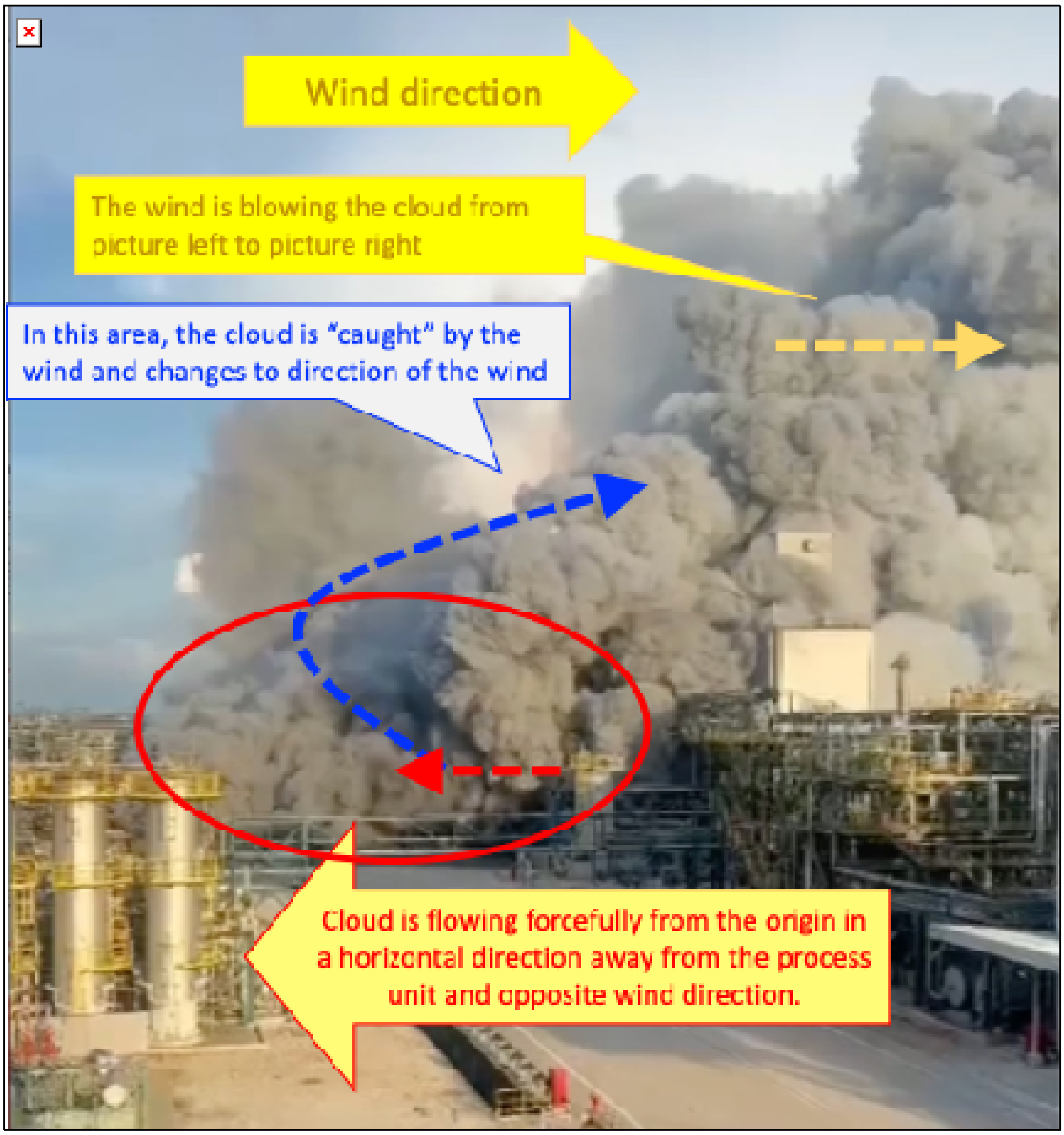
The video clearly shows that the origin of the "cloud" and, therefore, the loss of pressure containment of the process is near the ground. The "cloud" identified in Figure 7 with the red arrow is being discharged at a considerable velocity horizontally away from the process unit. After flowing perhaps 15 – 25 meters horizontally away from the origin, the cloud begins to rise and is picked up by the prevailing wind (blowing from picture left to picture right).

This horizontal movement away from the unit provides strong evidence that the failure occurred in a high-pressure part of the process. Prior analysis of which process unit and the location within the identified process unit (previous section of this report) shows the failure occurred within (or near) the HC fluid bed reactor process tower. The HC reactor and associated equipment is definitely a high-pressure part of the HC process. Specific operating conditions of the OCIM HC reactor is not known but likely in the range of 20 – 30 barg.

The dark gray color of the cloud is a definite indication that the failure occurred in a part of the process directly connected to the HC fluid bed reactor or even the reactor itself. This provides a very large "inventory" of reaction mass / MG-Si to discharge to the atmosphere. Experience also shows that when there is loss of pressure containment in a MG-Si containing section of any process, including HC, the high velocity discharge of gas and solids combined with the very abrasive characteristic of MG-Si usually increases the size of the original leak due to metal erosion.

A list of possible failure locations in the area associated with the bottom of the HC FBR along with explanations of why and how the specific areas could fail is provided in a later section of this document.

Figure 7: Screen shot at the 11 second mark of a social media posted video of the OCIM August 2024 fatal accident. Analysis of how the "cloud" is moving is provided.



Which Hydrochlorination process unit was involved in the Accident?
The previous two sections have provided strong evidence:

1) OCIM August 2024 fatal accident occurred in one of the Hydrochlorination (HC) ($Si + 2H_2 + 3SiCl_4 = 4HSiCl_3$) trichlorosilane (TCS: $HSiCl_3$) synthesis units.

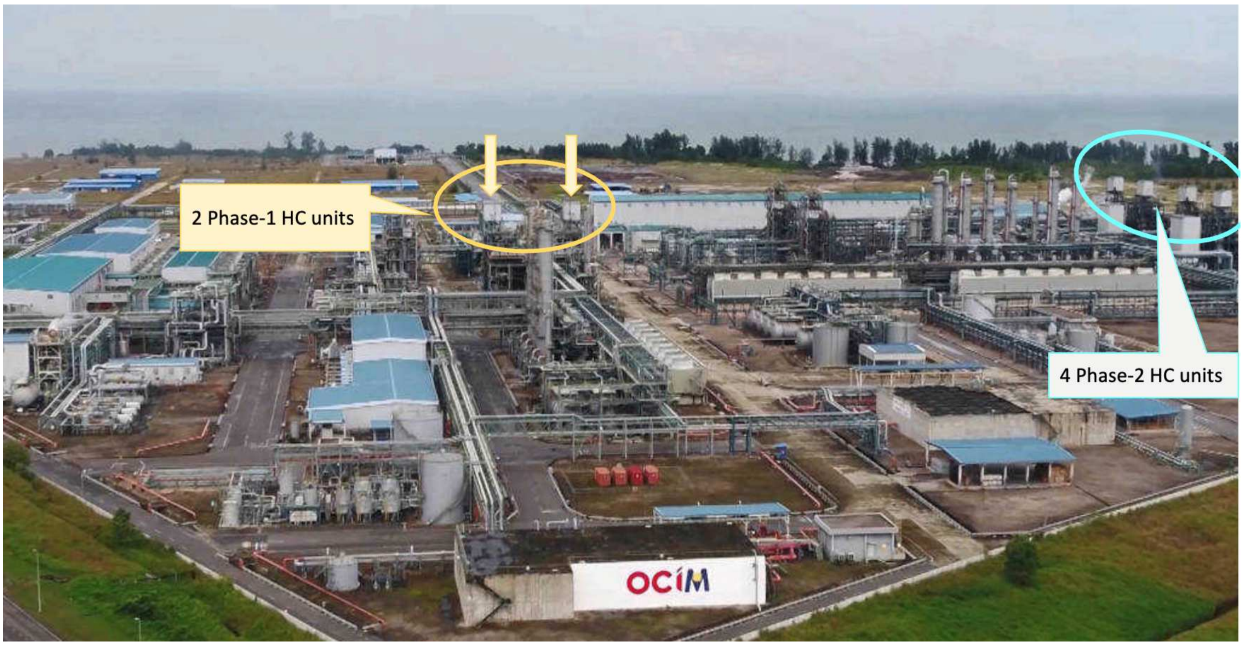
2) The accident occurred in the HC fluid bed reactor process tower

3) The accident occurred in the bottom area of the HC fluid bed reactor.

The OCIM site was originally constructed in two "Phases" by Tokuyama. Details of the known site history are provided in Appendix A. Phase-1 was built with two HC process units and Phase-2 was built with four HC process units. An assumption is made that the six HC units are identical design and capacity.

The original source of all HC technology used by Tokuyama was a USA company to be called "Company A" in this document. The HC technology of Company A was similar to the original Union Carbide Moses Lake, Washington, USA HC units. This comment is based on first-hand experience with HC technology supplied by Company A at KAM (South Korea). Figure 8 shows an aerial view of the OCIM site (taken from the OCIM web page) showing Phase-1 and Phase-2 locations. Phase-1 and Phase-2 locations are known from site analysis during the Tokuyama era.

Figure 8: OCIM site with Phase-1 and Phase-2 identified. Note the unique configuration of the six HC units: two in Phase-1 and four in Phase-2.



The accident location conclusions listed above are sufficient to proceed with analysis of what specifically could have failed and why the failure occurred, but there is a final piece of information that can be useful. This final information is to identify the specific HC process unit involved in the accident. This information is useful as there can be different operating histories of individual HC process units. These operating histories, while not possible to know without having access to confidential OCIM site history, could contribute to the accident root cause. The operating history of multiple HC process units on any industrial site can be unique to specific units. For example, one or more HC units may have significantly higher overall total operating time than other units resulting from staggered initial site startup or different operating rates resulting from polysilicon markets.

The additional analysis shows with a high degree of confidence that the 14-August-2024 accident occurred in one of the four original HC units associated with the original Tokuyama Phase-2 plant. Figure 1 and Figure 6 clearly show three HC units as evidenced by the enclosed MG-Si feed system (rectangular light-colored enclosure) located above the top of the HC reactors. Figure 8 shows the two HC units of Phase-1 (near the center of the photo and the four HC units of Phase-2 (background on the right corner of the photo). One can conclude with 100% certainty that the three HC units visible in Figure 1 and Figure 6 are from Phase-2. The fourth HC unit is not visible.

Tokuyama built Phase-1 and Phase-2. When OCIM purchased the site from Tokuyama, OCIM focused initial restart on Phase-2. The Phase-1 units eventually were restarted and significant “debottlenecking” occurred across the entire plant site (see Appendix A for details). OCIM eventually built (2019-2020) at least one and likely two new HC units. These new OCIM-installed HC units were installed adjacent to the original four HC units of original Phase-2.

Summary: Identification of OCIM August 2024 Fatal Accident Location

Analysis has been presented in this section of the document to show, with a high degree of confidence, that the accident occurred in the following location. The analysis combined photographs and video of the accident with experience of the author in design and operation of industrial trichlorosilane (TCS; HSiCl3)-based polysilicon plants with TCS produced by the Hydrochlorination (HC) reaction ($Si + 2H_2 + 3SiCl_4 = 4HSiCl_3$).

1) The August 2024 accident occurred in a HC process unit.

2) The August 2024 accident occurred in the bottom area of the HC reactor process tower which is the central part of an overall HC process unit.

3) The accident in occurred in one of the four HC process units originally built by Tokuyama as Phase-2 of the site.

Relevant Background Information on the Industrial TCS Synthesis Hydrochlorination Process ($Si + 2H_2 + 3SiCl_4 = 4HSiCl_3$)

The next sections:

1) Hydrochlorination unit process description
2) Fluid bed reactor introduction
3) Hydrochlorination Unit Materials of Construction
4) Make-up Chlorine Sources
5) Ground Metallurgical grade silicon Particle size distribution

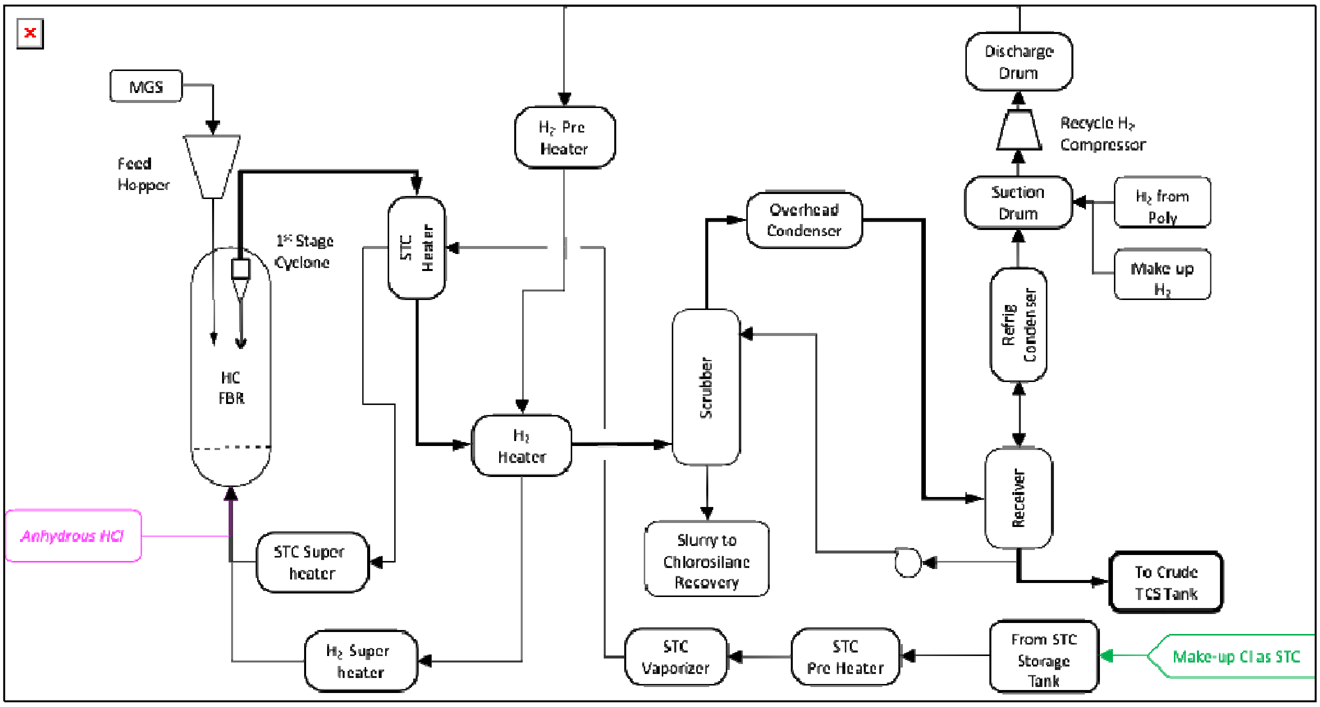
provide necessary and relevant background information about design, operation and maintenance of an industrial HC process unit. This section focuses on the HC process unit as experience-based analysis of the August 2024 accident photos and video clearly indicate the HC unit as the location of the accident.

Understanding this information is necessary to understand the analyses of the possible causes of the OCIM fatal accident.

TCS Synthesis Hydrochlorination Unit Process Description
The purpose of any industrial hydrochlorination (HC) process unit is to convert metallurgical grade silicon (MG-Si) to impure (sometimes called "crude") trichlorosilane (TCS; $HSiCl_3$) by means of the HC reaction ($Si + 2H_2 + 3\ SiCl_4 = 4HSiCl_3$). The HC process includes a complex arrangement of process vessels, heat exchangers, piping, instrumentation and process controls to produce TCS from MG-Si. While the focal point of the HC process unit is the HC fluidized bed reactor, additional unit operations are required.

Figure 9 provides a block flow diagram of a typical HC process unit found in a TCS-based polysilicon plant. The main process equipment and connecting piping is provided in Figure 9. Each specific HC unit can have a unique design that includes variations to the general design provided in Figure 9 but the end result is the same: MG-Si is converted to crude TCS.

Figure 9: Block flow diagram of general HC process unit present in a TCS-based polysilicon plant. This design assumes that all co-feed of anhydrous HCl (A-HCl) is to the HC reactor. A-HCl feed design can vary from that shown.



The HC process is operated continuously (24 hours per day; 7 days per week) for many months assuming normal operation. Some HC units may only run 3 months and others could run 12 months. Operation beyond 12 months is usually not found as various process safety protocols require periodic internal inspections of critical equipment and the maximum time between these inspections is usually 12 months. Some HC units could run longer than 12 months while others can never run 12 months. One leading cause of less than 12 month operation is a range of solids deposition (called fouling) inside various process equipment and piping. The plant operator would like to maximize HC unit run time as any outage (planned or unplanned) results in lost production and higher maintenance costs. Specific process design features and technology to enable maximized run times are closely guarded trade secrets.

The process starts with the HC fluidized bed reactor (FBR). The purpose of the HC FBR is to facilitate the reaction of solid, ground MG-Si powder, superheated hydrogen (H_2) gas, superheated silicon tetrachloride (STC; $SiCl_4$) vapor and anhydrous HCl to produce crude TCS. FBR's are the most efficient reactor design for gas – solid reactions. Depending on the physical size of the FBR, the fluidized bed of ground MG-Si (usually called the "reaction mass") can be 10 to over 50 metric tonnes. Typical operating conditions of the HC FBR are 525 – 575^{o}C and 20-30 barg.

Ground MG-Si powder is transferred from a large ground MG-Si storage silo to the HC process unit. MG-Si feed can be to the top or side of the HC reactor. Figure 9 shows one MG-Si feed hopper; the actual plant design requires two. A "low-pressure" hopper receives ground MG-Si from the storage silo. The contents of the "low-pressure" hopper are transferred to a "high-pressure" hopper located directly below. Ground MG-Si powder in the high-pressure hopper is periodically fed to the HC reactor by pressure. Sometimes an external copper catalyst is blended with the MG-Si powder for use in increasing TCS yield. The HC reaction does not require use of copper catalyst as impurities present in the MG-Si provide necessary reaction catalysis / promotion.

A. <u>HC FBR gas feed systems</u>

The HC FBR requires feed of superheated H_2 and STC. When an overall HC process unit is inspected, the equipment and piping associated with handling and heating the H_2 and STC feed streams comprises the most significant part of the process unit design. The H_2 and STC feed systems are a large "loop". This loop will be discussed in the following paragraphs before proceeding with the overall production and recovery of crude TCS product. The H_2 and STC gas feed heating system is required because the HC reaction is slightly endothermic; A-HCl co-feed can push the overall reaction to slightly exothermic depending on how much A-HCl is used. HC FBR's normally do not use internal heaters. As a result, the majority of the heat energy required for the HC reaction to occur is introduced via the H_2 and STC feeds.

1) *Hydrogen Feed System*

H_2 feed to the HC FBR has three origins that all start with the recycle H_2 compressor "Suction Drum" indicated in Figure 9. The first is the excess H_2 that was fed to the HC FBR that did not react. This excess H_2 is recovered in the "tail-end" of the HC unit (to be described later in this section). The "Suction Drum" is directly connected to the process unit that discharges this stream of H_2.

The second origin of H_2 in the HC FBR feed is H_2 recovered from the TCS-based Polysilicon production reactor off-gas recovery (OGR) unit of the plant (The Polysilicon production unit and off-gas recovery unit are indicated in Figure 3). Some excess H_2 recovered from the OGR can be returned to the HC unit. The normal entry point for this source of H_2 is the recycle H_2 compressor “Suction Drum” indicated in Figure 9.

The third origin of H_2 in the HC FBR feed is make-up H_2 supplied by a fence-line H_2 production company. Some H_2 is lost in various waste streams from the overall polysilicon plant and the lost must be replaced as “make-up”. Make-up H_2 is more typically added to the TCS-based polysilicon production reactors feed streams but could also enter the HC unit. The normal entry point for make-up H_2 is the recycle H_2 compressor “Suction Drum” indicated in Figure 9.

The three combined sources of H_2 are compressed by the “H_2 Recycle Compressor” to a pressure higher than the HC FBR operating pressure. H_2 is discharged from the compressor into a “Discharge Drum”. At this point, the goal for the H_2 feed system is to increase the temperature of the H_2 stream from near ambient to a value higher than the desired HC FBR operating temperature. There are numerous process designs to heat H_2; Figure 9 shows one possible design.

Cold H_2 flows from the “Discharge Drum” to the “H_2 pre-heater”. The H_2 pre-heater is a simple heat exchanger that raises the temperature of cold hydrogen to an intermediate level. The heat source of the “H_2 pre-heater” could be steam, heat transfer oil or cross exchange with a higher temperature process stream that needs to be cooled.

The pre-heated H_2 then flows to a second pre-heater or simply “H_2 Heater”. The H_2 heater shown in Figure 9 is a more complex heat exchanger that recovers “waste heat” from the HC FBR / cyclone off-gas stream by “cross-exchange”. The “waste heat” recovered from the HC FBR / cyclone off-gas stream raises the temperature of the H_2 feed gas. The term “waste heat” is used as the temperature of the HC FBR / cyclone off-gas stream is too high and offers “free” energy to raise the H_2 temperature.

H_2 discharge from the “H_2 Heater” finally flows through the “H_2 Superheater”. The purpose of the “H_2 Superheater” is to raise the temperature of the feed H_2 to the final desired value which is normally higher than the desired HC FBR operating temperature. There are a wide range of superheater designs (H_2 and STC superheaters) and selection of the proper design can be very important with regards to overall reliable and safe HC unit operation. Given the high desired exit temperatures (550 – 575+^{o}C), H_2 (and STC) superheaters normally use electric heating elements. It is possible to use natural gas or fuel oil direct fired superheater designs.

At this point, the required H_2 feed to the HC FBR has been properly heated.

2) *STC Feed System*

STC feed to the HC FBR begins as liquid STC stored in one or more STC storage tanks. The STC storage tanks receive liquid STC from two main sources within the polysilicon plant. There are two additional minor sources of STC.

The first main STC source is the TCS purification train (See Figure 3). An early purification step is to separate unreacted STC from the crude TCS product stream produced in the HC unit. This stream of unreacted STC is transferred from the TCS purification train to the STC storage tanks.

The second main STC source is from the TCS-based Polysilicon production reactor off-gas recovery (OGR) unit of the plant (The Polysilicon production unit and off-gas recovery unit are indicated in Figure 3). When polysilicon rods are produced from chemical vapor deposition of TCS reacting with H_2 in the "Siemens" reactors, STC is produced as a significant reaction by-product. The OGR unit of the polysilicon plant receives all combined off-gas streams from the many (20 – 50+ depending on plant polysilicon capacity) TCS "Siemens" reactors and separates this complex stream into the pure components. The STC by-product is one of these pure streams coming from the OGR. This STC stream also enters the STC storage tanks.

There are two additional sources of STC for feed to the HC FBR. The first is STC recovered from at least one waste stream generated in the HC unit (see below for additional information). The second is STC purchased by the polysilicon producer from external supplier(s) to be used as a source of make-up chlorine. Just as the overall polysilicon plant has H_2 losses (described in the H2 feed system section above), there are also chlorine (Cl) losses. One source of make-up chlorine is purchased STC. Additional details about make-up chlorine are presented later in this document.

The combined liquid STC is transferred to the STC heating system by use of high pressure STC feed pumps. At this point, the goal for the STC feed system is to increase the temperature of the STC stream from near ambient to a value higher than the desired HC FBR operating temperature (the same or similar temperature as for H_2). There are numerous process designs to heat STC; Figure 9 shows one possible design.

Liquid STC is pumped through the "STC pre-heater". The STC pre-heater is a simple heat exchanger that raises the temperature of liquid STC to an intermediate level. The heat source of the "STC pre-heater" could be steam, heat transfer oil or cross exchange with a higher temperature process stream that needs to be cooled.

The pre-heated liquid STC then flows to the "STC Vaporizer. The purpose of the "STC Vaporizer" is to vaporize the liquid STC to produce a saturated STC vapor stream. The energy source for the "STC Vaporizer" is usually heat transfer oil or steam; electric heating can be used. Some process configurations (not that in Figure 9) use a cross exchanger (with the HC / FBR off-gas stream) as the "STC Vaporizer".

Saturated STC vapor flows from the vaporizer to the "STC Heater". The STC heater shown in Figure 9 is a more complex heat exchanger that recovers "waste heat" from the HC FBR / cyclone off-gas stream by "cross-exchange". The "waste heat" recovered from the HC FBR / cyclone off-gas stream raises the temperature of the STC vapor. The term "waste heat" is used as the temperature of the HC FBR / cyclone off-gas stream is too high and offers "free" energy to raise the STC temperature.

STC discharge from the "STC Heater" finally flows through the "STC Superheater". The purpose of the "STC Superheater" is to raise the temperature of the feed STC to the final desired value which is normally higher than the desired HC FBR operating temperature. There are a wide range of superheater designs (H_2 and STC superheaters) and selection of the proper design can be very important with regards to overall reliable and safe HC unit operation. Given the high desired exit temperatures (550 – 575+^{o}C), STC (and H_2) superheaters normally use electric heating elements. It is possible to use natural gas or fuel oil direct fired superheater designs.

At this point, the required STC feed to the HC FBR has been properly heated.

- Some HC process units have started to use combined STC and H_2 superheaters instead of the separate superheaters described in Figure 9. The reason to combine the STC and H_2 superheaters is to save on capital investment. A combined superheater in Figure 9 would receive separate streams of STC from the "STC Heater" and H_2 from the "H_2 Heater". Figure 16 in a later section of this document provides a flow sheet showing the combined superheater.

A combined stream of superheated H_2 and STC is fed to the bottom of the HC FBR underneath the internal FBR grid plate. A-HCl co-feed is typically (there are other configurations which will be discussed later in this section) added to this combined H_2 and STC main gas feed. There are no known designs that add A-HCl upstream of the superheaters.

The grid plate keeps most MG-Si powder (reaction mass) from entering the HC FBR bottom head and, at the same time, distributes the main gas feed (H_2, STC, A-HCl) into the reaction mass through a number of specially designed individual holes.

The FBR normally includes an internal first stage cyclone located near the top. The purpose of the cyclone is to capture coarser solids that are entrained from the reaction mass in the combined stream of gas (unreacted H_2, unreacted STC and TCS product) that exits the FBR reaction mass. The coarser solids are returned to the reactor while the "off-gas" and finer solids exit the HC FBR / cyclone. The next section of this document provides additional details about FBR's.

The next step of the HC process is to recover some amount of the energy present in the hot off-gas stream that exits the HC FBR / cyclone. The energy is recovered by passing the hot off-gas stream through one or more "cross-exchangers". Figure 9 shows two cross-exchangers: 1) STC heater and 2) H_2 heater. Some HC designs may use only one cross exchanger and some could use more than two. Few, if any, modern, large capacity HC units are operated with no cross exchangers as doing so would represent a loss of recoverable energy resulting ultimately in higher operating cost (OPEX). Operation details of these cross exchangers have already been discussed in the "H_2 Feed System" and "STC Feed System" sections.

The next main step of the HC process combines three operations that are accomplished in one process system.

1) Remove the remaining entrained MG-Si / reaction mass "fines" from the off-gas stream (unreacted H_2, unreacted STC and TCS product).

2) De-sublime aluminum chloride ($AlCl_3$) vapor to solid $AlCl_3$. $AlCl_3$ is a nasty by-product produced in the HC reactor from reactive aluminum (Al) present in the MG-Si.

3) Cool (quench) the hot off-gas.

These three operations are accomplished in a vessel typically called a scrubber. There are alternate names for the scrubber and, in some cases, alternate process designs compared to what is shown in Figure 9. Regardless of name or configuration, the overall purpose to carry out these three operations is the same.

The scrubber operates by adding the fines-containing off-gas to the bottom of the scrubber. The bottom of the scrubber is designed to operate with a pool of liquid (condensed chlorosilanes). This liquid serves as the off-gas temperature quench, fines removal and $AlCl_3$ de-sublimation. Gas exiting the pool of liquid flows upward through the scrubber. Inside the scrubber are several "trays" or sometimes "packing". Solids-free chlorosilanes (STC and TCS) are added to the top of the scrubber as pumped reflux. These scrubber internals combined with the downward flowing solids-free chlorosilanes "scrub" out the "fines" from the off-gas.

A bottoms stream is removed from the "Scrubber". This stream contains all recovered MG-Si / reaction mass "fines", solid $AlCl_3$, liquid chlorosilanes (mostly STC but also some TCS and polychlorosilanes such as Si_2Cl6) and other higher boiling impurities. The "Scrubber" bottoms stream is usually called "slurry". The slurry is transferred from the high-pressure HC unit to the chlorosilane recovery process unit (not shown in Figure 9) through a series of holding vessels.

The purpose of the chlorosilane recovery process is to separate a portion of the valuable chlorosilanes present in the slurry from the solids. The recovered chlorosilanes are recycled back to the main STC storage tank(s). The remaining solids (and some residual chlorosilanes) are extremely reactive and pyrophoric. These solids must be neutralized and converted to a safe, stable solid. The neutralized solids are normally transferred to an approved landfill.

The gas stream exiting the top of the scrubber should be free of entrained MG-Si / reaction mass "fines" and $AlCl_3$ (in practice, there is always some $AlCl_3$ present). This clean (solids-free) gas stream of unreacted H_2, unreacted STC and TCS product (there is also a small amount of dichlorosilane [DCS; H_2SiCl_2] “product”) exist the scrubber and flows into the “Overhead condenser”. The “Overhead Condenser” can use air or cooling water and can be one or more individual heat exchangers. Most of the STC and TCS is condensed from vapor to liquid in the “Overhead Condenser”.

The combined gas and liquid discharge from the “Overhead Condenser” flows to the “Receiver”. The “Receiver” is a vertical tank that allows separation of gas from liquid. The liquid, which contains unreacted STC, TCS product and small amounts of DCS product is transferred by pressure to the “Crude TCS Storage Tank(s)”. A portion of the liquid is also pumped from the “Receiver” as reflux back to the top of the “Scrubber”. The “Crude TCS Storage tank(s)” serve as the feed point to the TCS purification section of the polysilicon plant (see Figure 3). As noted, the unreacted STC present in the crude TCS is recovered in the TCS purification section, transferred to the “STC Storage tank(s)” and re-fed to the HC FBR.

The gas portion of the “Overhead Condenser” exit stream flows out of the top of the “Receiver” to the final condensation system. Figure 9 shows one “Refrigerated Condenser”. Some industrial HC units may use one condenser while others may use several. A suitable refrigerant passes through this heat exchanger with the goal of condensing the remaining chlorosilanes present in the gas stream. The condensed chlorosilanes (mostly TCS and some DCS; just traces of STC) flow back to the “Receiver” and are combined with the liquid chlorosilanes.

The cold gas exiting the “Refrigerated Condenser” is primarily unreacted H_2. The H_2 may also contain small amounts of low boiling impurities including nitrogen (N_2), HCl and hydrocarbons. To prevent accumulation of these impurities, there is usually a small purge stream directed to a suitable vent scrubber (not shown in Figure 9). The “Refrigerated Condenser” off-gas stream flows to the “Recycle H_2 Compressor” “Suction Drum” where the other two H_2 streams are added.

The process description of the HC process does not include mention of minor process details nor required process vent scrubber(s) and safety systems.

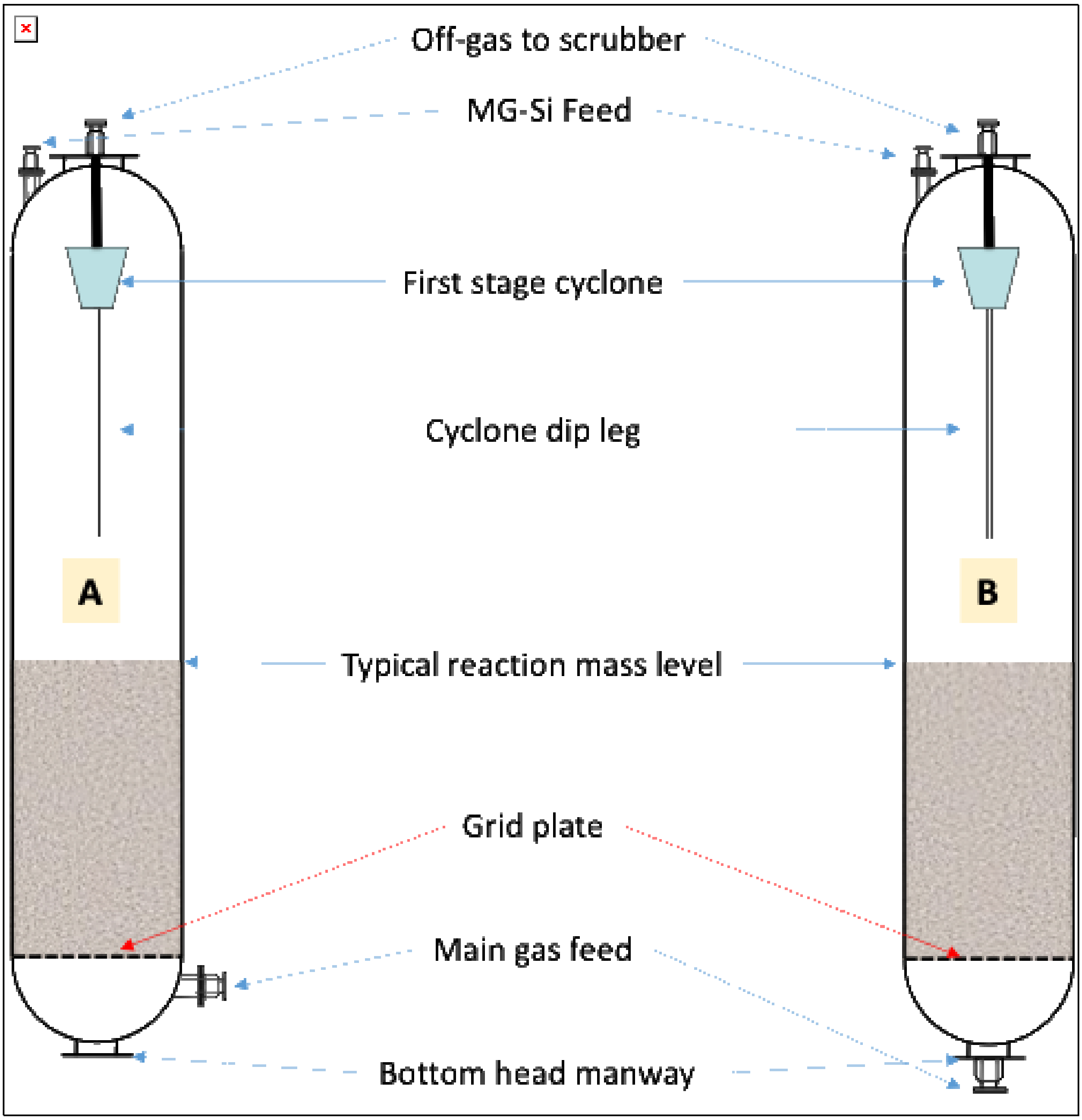
Fluid Bed Reactor Introduction
The hydrochlorination (HC) ($Si + 2H_2 + 3SiCl_4 = 4HSiCl_3$) reaction is conducted in large fluid bed reactors (FBR's). A FBR is a vertical, cylindrical vessel that has a bottom "grid" plate. The FBR is designed to facilitate efficient chemical reaction between a fine solid and gas. For the HC reaction, the fine solid is ground metallurgical grade silicon (MGS) and the gas is a mixture of superheated hydrogen (H_2), silicon tetrachloride (STC; $SiCl_4$) and, in the case of trichlorosilane (TCS; $HSiCl_3$) based polysilicon, some amount of anhydrous hydrogen chloride (A-HCl). A general drawing of a HC FBR is provided in Figure 10.

MGS lump is ground to a very specific particle size distribution (PSD). The ground MGS is fed to the reactor above the grid plate. H_2, STC and, depending on specific design, A-HCl is fed to the bottom of the reactor below the grid plate. The grid plate contains many holes of specific diameter and design. The holes distribute the feed gas into the "bed" or "reaction mass" of ground MGS. The holes are also designed to minimize "sifting" of the ground MGS powder into the area under the grid plate. The gas "fluidizes" the ground MGS and the HC chemical reaction occurs. The fluidized bed of ground MGS behaves like a liquid; if a hole or breach of the FBR vessel were to occur, the fluidized ground MGS contents would be discharged from the reactor just like a liquid. Ground MGS powder is extremely abrasive and great care is usually taken in the mechanical design of the ground MGS feed system and specific components of the HC FBR and downstream piping to minimize internal erosion caused by impingement of the abrasive MGS on any internal surface.

Industrial HC FBR's operate at about 550^{o}C and at a pressure normally of 20 to 30 barg (depending on specific reactor design). Modern HC FBR's can have diameters greater than 3 meters and overall heights greater than 40 meters. The HC FBR's can easily contain 80 to 100 metric tonnes of ground MGS during steady-state operation. The only proven material of construction of the HC FBR and all internal components is Incoloy 800H (UNS N08810).

An industrial HC FBR is designed to operate within a very narrow set of process conditions. The main design parameters are total gas (H_2, STC, A-HCl) flow rate into the reactor and particle size distribution (PSD) of the ground MGS. Safe and optimum HC FBR operation requires careful adherence to the design parameters. Intentional or unintentional deviation from the design parameters can result in serious operational problems that can lead to serious safety problems. An industrial HC FBR has very limited "turn-down". Fluidization is a very complex topic and experience shows that even the best operators of HC units can struggle to maintain optimum operation, especially with the current very large HC FBR's.

Figure 10: General elevation drawing of an industrial hydrochlorination fluid bed reactor. The main components are included. Two configurations are provided for feed of the main superheated gas to the reactor. Configuration “A” shows the main gas stream entering at the side of the bottom head. Configuration “B” shows the main gas stream entering at the bottom. Reactor diameters can range from 1 meter to over 3 meters. Overall heights are greater than 9 meters.



Hydrochlorination Unit – Materials of Construction
As with any industrial chemical plant, a hydrochlorination (HC) trichlorosilane (TCS) synthesis unit requires use of unique materials of construction. Selection of the wrong materials of construction for any chemical process unit can easily result in accelerated failure of the equipment (piping and / or vessels) due to internal corrosion caused by the chemicals being handled.

One of the main sections of the HC process unit requiring unique / specialized materials of construction is the HC fluid bed reactor (FBR) vessel (along with all internals) and piping and equipment immediately upstream and downstream of the HC FBR vessel. The material of construction of choice for these parts of the HC unit is Incoloy 800H (UNS N08810). The Union Carbide centric selection of Incoloy 800H is discussed below.

Information about development of HC process technology in Japan is not available. There are three long-term Japanese operators of industrial HC units: Denal, Osaka Titanium (formerly Sumitomo; no longer operating) and Tokuyama. Material of construction used by these Japanese HC operators is not known.

A. Union Carbide Summary

Union Carbide selected Incoloy 800H as the material of construction of the HC FBR vessel beginning with construction of a small scale HC reactor as part of the overall silane pilot plant built in Washougal, Washington, USA (this pilot plant was built and operated prior to building the full scale silane plant in Moses Lake, Washington, USA). Selection of Incoloy 800H by Union Carbide followed a process that combined the strong materials / metallurgy / vessel fabrication expertise found internally within several Union Carbide divisions and several laboratory scale corrosion studies. The known process conditions of the HC reaction were combined with these technical resources. The result was selection of Incoloy 800H as the material of construction of the HC FBR vessel.

While the Union Carbide project to build a silane plant was documented by a large number of publications (this was a requirement as some funding came from the US government through the Jet Propulsion Laboratory low-cost solar array project), detailed information about how Incoloy 800H was selected was never published. The only public domain direct Union Carbide acknowledgement that Incoloy 800H was the recommended material of construction can be found in one reference: *Low Cost Solar Array Project. Feasibility of the silane process for producing semiconductor-grade silicon. Final report, October 1975-March 1979*. United States: N. p., 1979, p. 45. See: https://www.osti.gov/biblio/5535914

B. Incoloy 800H Dissemination from Union Carbide

The use of Incoloy 800H as the preferred material of construction for the HC FBR vessel and associated piping is very common knowledge as of late 2024. How the use of Incoloy 800H became "common knowledge" is not clear. As noted in the prior section. Union Carbide was very selective in public disclosure of their use of Incoloy 800H. One can assume that this public recommendation combined with the gradual disclosure / confirmation of Incoloy 800H use by former Union Carbide and Advanced Silicon Material employees, EPC firms (Rust [used for the original Moses Lake design] and Foster Wheeler [Butte]) and vessel fabricators eventually led to the widespread knowledge.

An example of "recent" public disclosure of Incoloy 800H use can be found from a document that was posted on the web site of Verolme Special Equipment b.v. (Rotterdam, Netherlands). Figure 11 provides an excerpt of the 2011 Verolme publication. Verolme was a leading fabricator of large Incoloy 800H vessels (HC FBR's and also ethylene crackers) that developed some special fabrication methods and a unique tighter specification for Incoloy 800H composition to address stress relaxation cracking. Verolme is no longer in business.

Figure 11: Excerpt from 2011 Verolme Special Equipment b.v. publication about use of Incoloy 800H for fabrication of HC FBR's.

VEROLME
Special Equipment b.v.
VSE

Leading industry experience

Verolme Special Equipment is a well-known partner of the leading companies in the Polysilicon industry. In the last decade we successfully delivered more than 2000 tonnes of pressure containing equipment to customers all over the world. We manufactured a high number of fluid bed reactors, special heat exchangers, hydrogenation & hydrochlorination reactors, and reactor effluent exchangers. This equipment has all been made of our proprietary grade of alloy 800H, known in the Polysilicon industry as Verolme 800H/HT Modified®. Our proven track record shows that all Verolme equipment functions properly, without any indication whatsoever of stress-relaxation-cracking (SRC) or other mechanical defects.

Fig. 3. Verolme 800H/HT Modified® Reactor

C. <u>Union Carbide Corrosion Studies</u>

Union Carbide conducted several corrosion studies through the course of the overall silane project. All of the corrosion studies followed similar experimental protocol. Results were included in several published reports including the referenced 1979 JPL report that recommended Incoloy 800H. The corrosion study in the 1979 report investigated (UNS numbers in parentheses) Incoloy 800H (N08810), Inconel 625 (N06625), Inconel 825 (N08825), 304 SS (S30400), 316 SS (S31600), 26-1 SS (S44627), Chrome plated Steel, Carbon steel (K02700), Titanium and 3RE60 Duplex stainless steel (S31500). Additional later studies included Hastalloy C276 (N10276), Monel 400 (N04400) and Hastalloy B2 (N10665).

The only publication outside of a JPL report of any Union Carbide corrosion work was from Jeff Mui; see Mui, J.Y., 1985. Corrosion mechanism of metals and alloys in the silicon-hydrogen-chlorosilane system at 500 C. *Corrosion*, *41*(2), pp.63-69. Mui was a chemist who originally worked for Union Carbide and ran lab programs for the hydrochlorination and redistribution (TCS to silane) reactions. Corrosion studies were included in the overall hydrochlorination lab reactor work. Mui later left Union Carbide and worked independently on the Union Carbide project through his company Solarelectronics.

The Mui report, following standard Union Carbide protocol, did not recommend a specific material. The Mui report provided results for the following materials of construction (UNS numbers in parentheses): Incoloy 800H (N08810), Hastalloy B2 (N10665), Monel 400 (N04400), 304 SS (S30400), Carbon steel (K02700), pure Nickel and pure Copper. Mui concluded that Incoloy 800H, Hastalloy B2 and 304 Stainless were acceptable materials. While not included in the *Corrosion* publication, Mui did mention in a JPL publication (that presented the original data used for the Corrosion publication) that 304SS was not as desirable due to a higher sensitivity to chloride corrosion. The most useful part of the Mui publication is his discussion of how Incoloy 800H is protected against corrosion. This is summarized in a separate section below.

D. <u>Union Carbide Incoloy 800H Boundary Limits</u>

The boundary limits of Union Carbide's Incoloy 800H selection are very important to understand. Most current (late 2024) "new" (since the early 2000's) industrial HC process unit operators likely do not appreciate the Union Carbide boundary limits.

All of the Union Carbide corrosion studies followed a similar experimental protocol. The most important part of the protocol was the "system" to be evaluated. Since the goal of these corrosion studies was to select a material of construction for the HC FBR vessel, the ONLY "system" considered by Union Carbide was Hydrogen – Silicon tetrachloride – Metallurgical grade silicon (H_2 – STC – MGSi). These are the components fed to the HC reactor. All of the laboratory corrosion studies were conducted in the laboratory scale HC reactor that was used to study the HC reaction. Operating conditions of the corrosion studies were 500^{o}C, 20.7 barg and 2:1 molar ratio of H_2 to STC.

All published Union Carbide documents that discuss corrosion ONLY consider the H_2 – STC – MGSi system. While Union Carbide may have considered the H_2 – STC system, there are no published discussions of this MGSi-free system. This is a very important, but subtle, distinction. All known industrial HC units operate with at least some amount of combined superheated H_2 – STC feed between the superheaters and the HC reactor main gas inlet. This main gas feed stream DOES NOT contain MGSi.

The off-gas stream from the HC FBR / first stage cyclone (if a cyclone is used) contains predominately unreacted H_2, unreacted STC and TCS product. Some entrained MGSi fines are present along with traces of anhydrous HCl and traces of other chlorosilanes such as dichlorosilane (DCS; H_2SiCl_2). This system in the off-gas can be considered close to the H_2 – STC – MGSi system present in the HC reactor. Additionally, due to the presence of entrained reaction mass "fines", not only must corrosion be considered but also erosion from the abrasive fines.

The Union Carbide corrosion studies only focused on the H_2 – STC – MGSi. These studies along with input from materials and vessel design experts resulted in the recommendation for using Incoloy 800H for the HC FBR vessel. There were NO corrosion studies for H_2 – STC (main gas feed to the HC reactor). The piping for the main gas feed to the HC reactor and the off-gas piping located between the HC reactor and inlet to the settler (scrubber) were also specified to be Incoloy 800H but this selection was not based on specific corrosion studies.

Union Carbide may have not considered corrosion of the H_2 – STC main gas feed system as the original Washougal, Washington, USA HC pilot reactor did not combine the superheated H_2 and STC before the bottom of the HC reactor; H_2 and STC entered the reactor via separate connections. The H_2 and STC streams were combined, after separate superheaters, beginning with the first Moses Lake reactor. The length of the combined H_2 – STC feed piping was short.

The H_2 – STC system in the combined main gas feed line to the HC reactor is best defined by the work of Hunt and Sirtl for the system Si – H – Cl (see: L. P. Hunt and E. Sirtl 1972 *J. Electrochem. Soc.* **119** 1741). Given the normal excess H_2 feed, the combined H_2 and STC system in the main gas feed line is in the HCl "etch" mode for the system. The short residence time of the combined gas feed line (at least in most industrial designs the combined gas feed pipe is very short) should limit internal corrosion.

The overall safe operations of Union Carbide / Advanced Silicon Materials (ASiMI) / REC Silicon in Moses Lake, Washington and Butte, Montana in these specific areas since the first HC reactor was started in 1985 would seem to confirm that the original selection of Incoloy 800H was correct. Hidden in this statement is the continuous, never-ending work by UCC / ASiMI / REC to ensure safe operations in this area via rigorous application of mechanical integrity programs and use of detailed operating, maintenance and return to service procedures.

A final important boundary limit for Union Carbide is the fact that routine industrial HC operation has never included use of anhydrous HCl (A-HCl) as a co-feed to the HC reactors along with H_2 and STC. All current (late 2024) HC operators that produce TCS-based polysilicon are co-feeding some amount of A-HCl. This is not within the original Union Carbide boundary limits and there are no public domain corrosion studies that include A-HCl. The next section of this document provides details about A-HCl co-feed.

Figure 12 shows provides a block flow HC process unit diagram that shows the overall use of Incoloy 800H. This overall Incoloy 800H use was true for the original Union Carbide pilot reactor operated in Washougal, Washington, USA and true for most of the new HC units built in 2024. Figure 13 shows the main compositions found in a typical HC unit (for silane production; no anhydrous HCl). Figure 14 provides a block flow HC process unit diagram that describes the Union Carbide corrosion study boundary limits and use of Incoloy 800H for the original Washougal, Washington, USA pilot reactor. Note the separate feed streams of superheated H_2 and STC. Figure 15 provides a block flow HC process unit diagram that describes the Union Carbide corrosion study boundary limits and use of Incoloy 800H for all industrial reactors in Moses Lake, Washington, USA and Butte, Montana, USA.

Figure 12: Block flow diagram of a typical HC process unit showing the general extent of Incoloy 800H use. This applies to the Union Carbide pilot HC reactor as well as most of the newest HC units built in 2024. Incoloy 800H areas are shown in blue; other materials are gray.

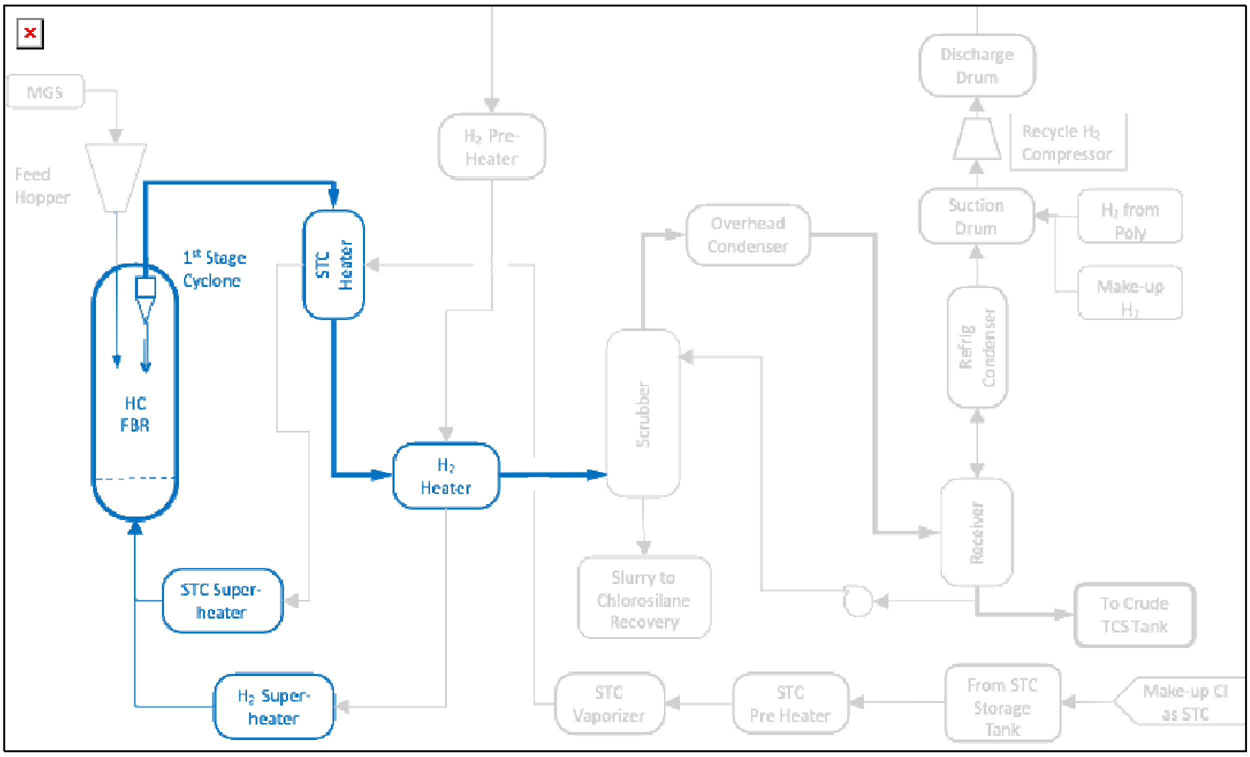


Figure 13: Block flow diagram of a typical HC process unit showing main compositions.
Where: Gray = MG-Si, H_2; Red = H_2; Blue = STC; Magenta = H_2, STC; Green = MG-Si, H_2, STC;
Orange = MG-Si, H_2, STC, TCS; Brown = H_2, STC, TCS; Gold = MG-Si, STC; Black = STC, TCS

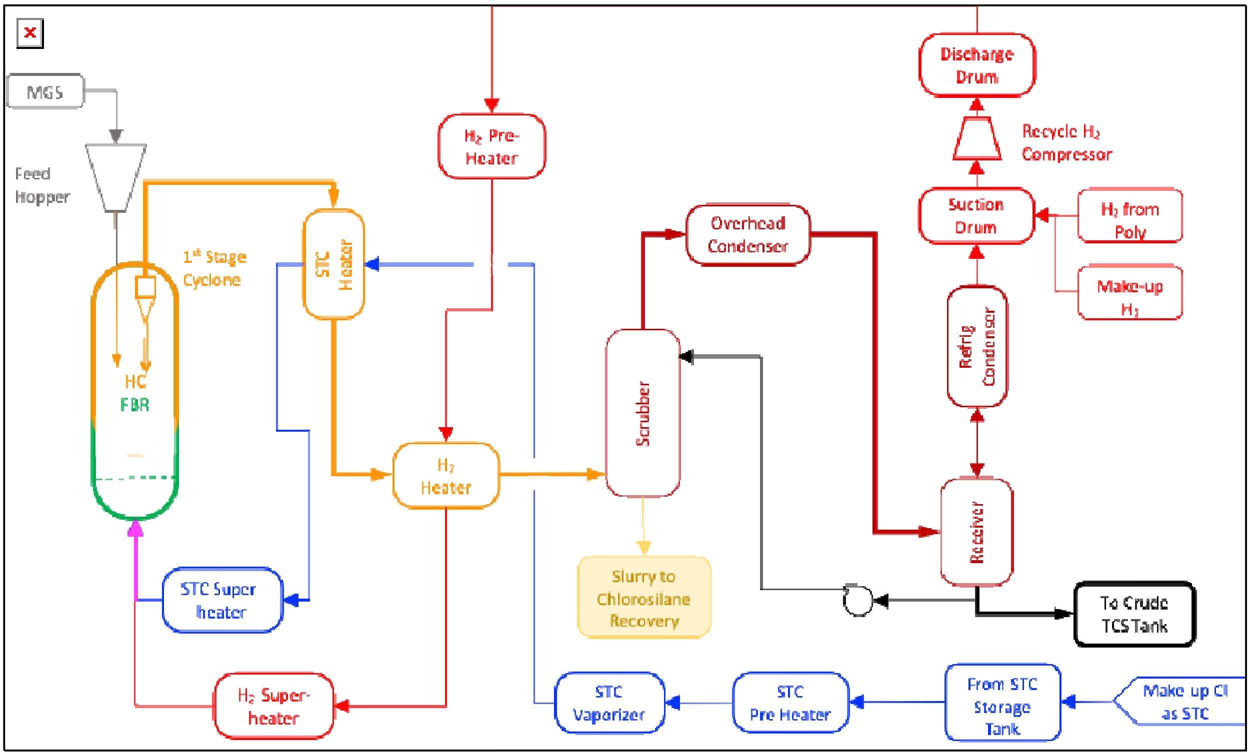


Figure 14 Block flow diagram of the Union Carbide pilot Hydrochlorination process unit used to produce TCS for production of silane (SiH_4). Note the separate feeds of H_2 and STC to the HC reactor. Anhydrous HCl co-feed is not required for a silane plant. The green highlighted equipment show use of Incoloy 800H based directly on Union Carbide corrosion studies with the system H_2 – STC – MGSi (these are the reactants fed to the HC reactor). The magenta highlighted equipment shows use of Incoloy 800H in a similar system as the HC reactor. The blue highlighted areas used Incoloy 800H but represent pure components (H_2 and STC) with limited corrosion concern. The gray sections do not use Incoloy 800H.

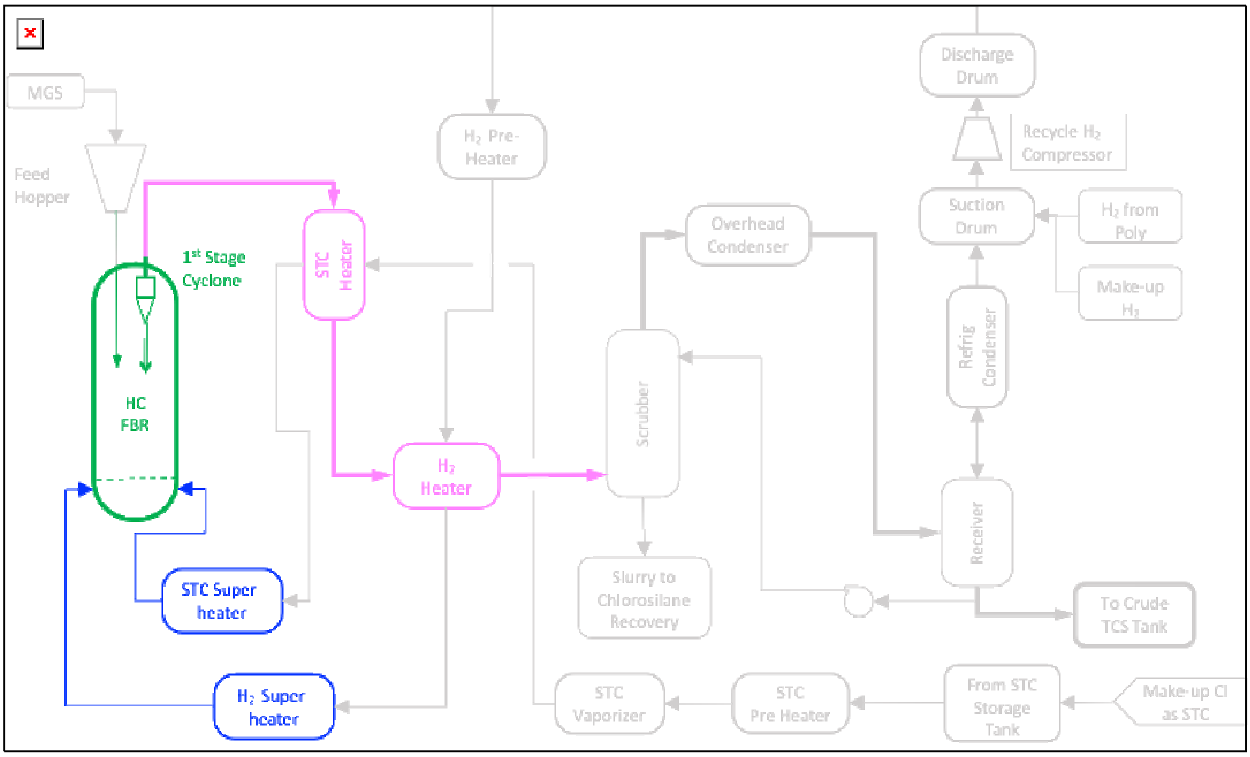
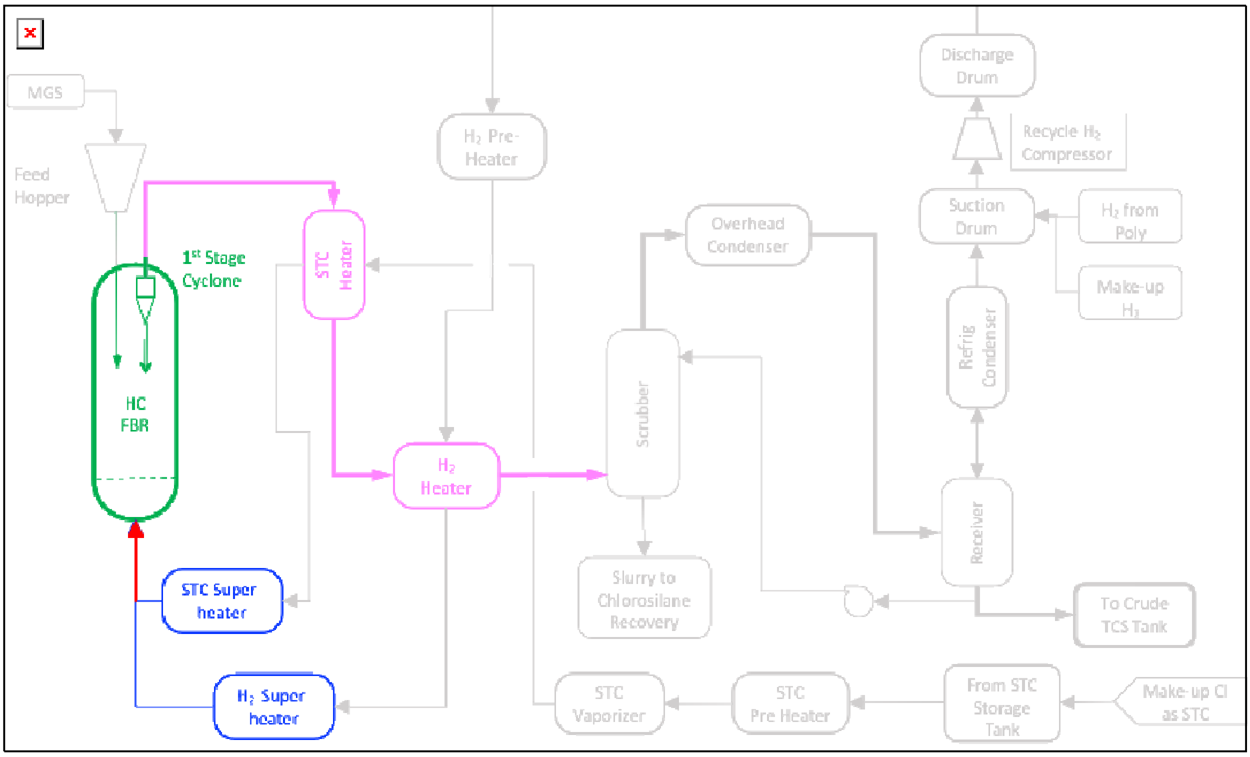


Figure 15 Block flow diagram of the Union Carbide industrial Hydrochlorination process unit used to produce TCS for production of silane (SiH_4). Anhydrous HCl co-feed is not required for a silane plant. The green highlighted equipment show use of Incoloy 800H based directly on Union Carbide corrosion studies with the system H_2 – STC – MGSi (these are the reactants fed to the HC reactor). The magenta highlighted equipment shows use of Incoloy 800H in a similar system as the HC reactor. The blue highlighted areas used Incoloy 800H but represent pure components (H_2 and STC) with limited corrosion concern. The red highlighted area shows use of Incoloy 800H for the H_2 – STC system which is not supported by any corrosion studies. The gray sections do not use Incoloy 800H.



E. <u>Union Carbide Incoloy 800H Corrosion Mechanism</u>

The Mui *Corrosion* publication provides an excellent hypothesis as to the method that Incoloy 800H is protected against corrosion, mostly from HCl. The hypothesis is supported by experimental SEM-EDX (Scanning electron microscope – energy dispersive X-ray) analysis to qualitatively identify protective layers formed within the HC reactor.

SEM-EDX work identified the protective layer found on the inside surface of Incoloy 800H test coupons as nickel silicide. Nickel silicide exists in several stoichiometries. The SEM-EDX analysis suggested the forms of nickel silicide as NiSi and Ni_3Si_2. Based on this work from the early 1980's, it has become "common knowledge" that Incoloy 800H is protected from corrosion via in situ formation of NiSi or Ni_3Si_2. Some with high experience in this area have hypothesized that the protective coating is really $NiSiCl_2$ instead of just NiSi. The $NiSiCl_2$ hypothesis is backed by observations of how the protective nickel silicide coating falls off when the HC reactor is open to atmosphere and exposed to moisture. First-hand experience of this document's author has observed solid scale "raining" down inside an industrial HC FBR that has been opened for routine maintenance. Qualitative testing of the scale showed high nickel content.

Mui discusses how the NiSi / Ni_3Si_2 is formed on the inside surfaces of the Incoloy 800H vessel. The formation is centered on the presence of a bulk amount of MG-Si inside the reactor.

Step-1: $Si + 2H_2 + 3SiCl_4 = 4HSiCl_3$ (the "normal" HC reaction)

Step-2: $4HSiCl_3 = Si + 2H_2 + 3SiCl_4$ (the reverse of the HC reaction)

- Additional sources of Si deposition can be decomposition of dichlorosilane (DCS; H_2SiCl_2 which is produced in small amounts) and decomposition of traces of silane (SiH_4) present in the H_2 that is recycled from the Silane Siemens or Silane FBR polysilicon section of the plant.

Step-3: Si from Step-2 is deposited on the wall of the reactor. The Si diffuses into the base metal of the reactor where it reacts with Nickel to form NiSi / Ni_3Si_2.

Step-4: When the reactor is opened to atmosphere and exposed to moisture the NiSi / Ni_3Si_2 reacts and is removed. This represents corrosion loss of Incoloy 800H. When the reactor is fully dried and returned to service, the NiSi / Ni_3Si_2 coating is replaced starting with Step-1.

- First-hand experience of this document's author has observed a buildup of pure Si on the inside surfaces of an industrial HC fluid bed reactor that has been opened for routine maintenance. The Silicon was prevalent on the walls just above the grid plate. The thickness was about 2 mm. This observation confirms the Mui hypothesis of Si deposition.

F. Incoloy 800H Concerns

The main concern with Union Carbide's selection of Incoloy 800H was the effect of water. Exposure to water during times when the Incoloy 800H equipment (reactor, heat exchangers, piping) were open to the atmosphere for maintenance was viewed as the highest corrosion causing risk. Water could enter either from humidity in the air or intentional equipment water washing. Water washing is commonly used in the chlorosilane and methylchlorosilane industry to prepare process equipment for maintenance but most of the equipment used in direct chlorination TCS synthesis or methylchlorosilane synthesis is constructed of carbon steel.
Water entering the internals of Incoloy 800H equipment reacts with residual solids and absorbed / adsorbed chlorosilanes to produce localized areas of strong aqueous HCl. If the Incoloy 800H equipment internal surfaces are not totally cleaned of residual solids and totally dried prior to being returned to service, the localized HCl can attack the base metal. This was a common failure mode of internal Incoloy 800H bellows seals used in

early Union Carbide designs of the cross exchangers used in the HC reactor off-gas piping (identified as STC Heater and H_2 Heater in Figures 5, 6, 7 and 8).

Given the water-related corrosion problems, safe use of Incoloy 800H in an industrial HC unit includes very detailed maintenance, inspection and return to service procedures that are always followed. Failure to ensure 100% clean and dry internal Incoloy 800H services can result in premature corrosive failure regardless of other measures taken by the plant operator.

G. Incoloy 800H vessel Corrosion Allowance

Union Carbide mechanical integrity testing data for the HC reactors constructed of Incoloy 800H show an approximate loss of 0.1 mm metal every time the HC reactor internals are exposed to atmosphere. Exposure occurs whenever the HC reactor is opened for maintenance and / or internal inspections. This corrosive loss is from the previously described corrosion mechanism of how the protective NiSi / Ni_3Si_2 (or $NiSiCl_2$) layer is formed and then subsequently "lost" upon exposure to moisture.

The original Union Carbide and ASiMI HC reactors were designed with conservative 6 mm corrosion allowance. Assuming the HC reactor is opened for internal inspections once per year and a 0.1 mm loss each time the reactor is opened, a 6 mm corrosion allowance enables 60 year vessel life! The assumption of one vessel opening per year, especially in the early days of industrial HC operation in Moses Lake is likely not accurate.

First-hand experience shows that most of the HC reactors that have been designed, built and installed in the large polysilicon plants in recent times (late 2000's through late 2024) are designed with 1 mm corrosion allowance. Assuming these reactors are also opened once per year and the same 0.1 mm loss each time the reactor is opened, the 1 mm corrosion allowance enables only a 10 year vessel life. Depending on the actual Incoloy 800H plate thickness used in fabrication of these reactors, there could be some "unaccounted" corrosion allowance present but use of this would require modification of vessel design calculations.

Perhaps a compromise reasonable corrosion allowance is 3 mm? Assuming the reactor is opened once per year and there is a 0.1 mm loss per opening, 3 mm corrosion allowance enables 30 year vessel life.

H. Non Corrosion Factors for Incoloy 800H Vessels

Incoloy 800H is the long term proven material of construction for HC fluid bed reactor vessels and associated feed and off-gas piping (provided the plant operator has a rigorous mechanical integrity program and detailed operating, maintenance and return to service procedures. There are additional factors that must be fully understood to enable safe operation. Failure to understand these factors can result in premature vessel or piping failure regardless of the overall policies and procedures used by the plant operator.

Fabrication of large industrial Incoloy 800H vessels and associated process piping requires a high level of competence of the fabricator(s). Many companies may claim to have Incoloy 800H experience but, first-hand experience shows that very few actually have the expertise required to ensure the lowest chance of fabrication related problems. Vessels (HC reactors, heat exchangers) fabricated from Incoloy 800H in the early (1980's and 1990's) periods of industrial use often experienced significant problems before the vessels were even placed in service. Some HC reactors delivered to Union Carbide and Advanced Silicon materials experienced significant weld cracks prior to being commissioned.

Details of Incoloy 800H fabrication are beyond the scope of this document but can be found in various references. A main problem associated with Incoloy 800H is stress relaxation cracking (SRC). SRC can be mitigated by proper fabrication techniques including post weld heat treatment and the details of how the vessel is assembled. SRC can also be mitigated by use of unique, tighter specifications of some impurities found in Incoloy 800H.

Several competent fabricators of large Incoloy 800H vessels are currently in operation around the world. There are many other fabrication shops that claim to have high Incoloy 800H experience but these should be avoided. Any company building industrial HC units must be very careful in selection of Incoloy 800H vessel fabrication shops.

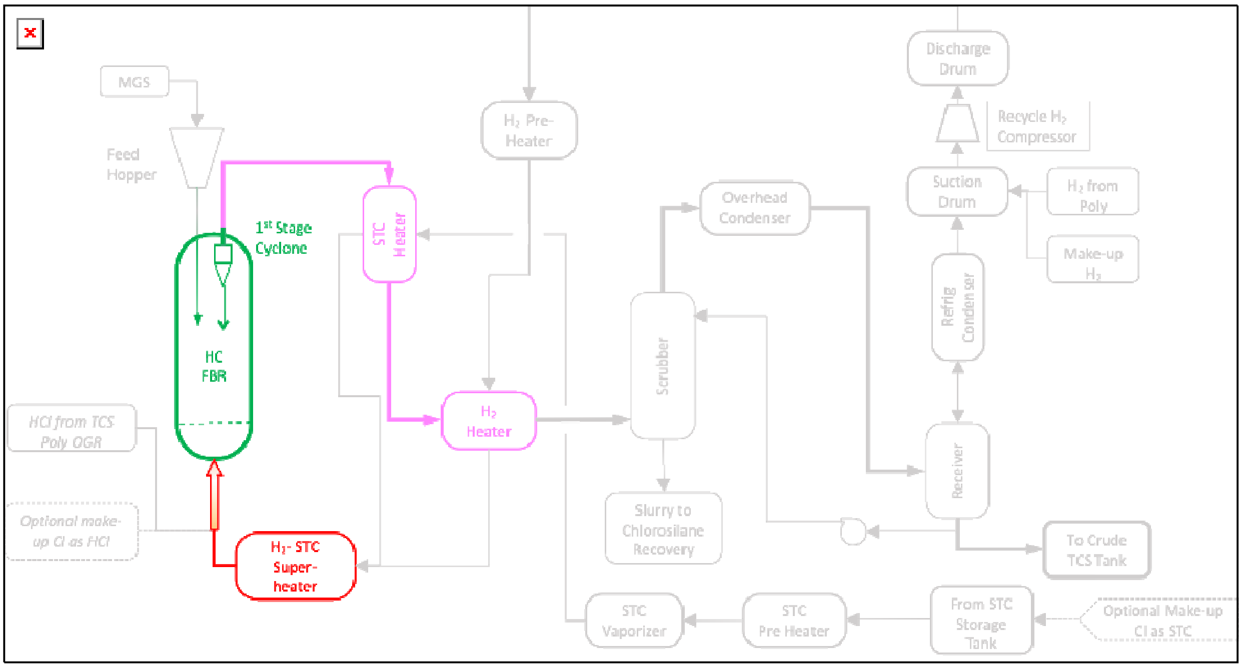
I. Recent Material of Construction Comments

There are no known public domain reports or other information published about relevant HC process since the 1985 Mui *Corrosion* article previously referenced. The massive use of HC as the front end of TCS-based solar grade polysilicon plants since the late 2000's combined with anhydrous HCl (A-HCl) co-feed (see next section in this document) have been met with zero updates on Incoloy 800H corrosion. Conservatively there is about 1,500,000 TPY solar grade polysilicon capacity (TCS-based Siemens and silane-based granular fluid bed reactor) in late 2024 that uses HC for synthesis of crude TCS.

The most concerning lack of updated published corrosion data is the widespread co-feed of A-HCl with superheated H_2 and STC, i.e. the system H_2 – STC – HCl. Figure 9 shows a block flow diagram of a HC unit showing the most common feed gas configuration. Note both A-HCl co-feed and combination of H_2 and STC superheating (H_2 – STC system or Hunt & Sirtl Si – Cl – H system in "etch" mode). Combining H_2 and STC superheating has the potential to introduce another corrosion risk factor based on operation in HCl "etch" mode. Superheaters can be electric (indirect radiant box or direct immersion) or gas / fuel oil fired (indirect radiant box design. If direct immersion style electric superheaters are used, depending on the specific design, surface temperatures of the electric heating elements can operate 150 – 200+°C higher than the desired final superheated gas temperature (~ 550-575°C). These significantly higher local temperatures, when applied to combined H_2 and STC superheating (A-HCl is NOT superheated; A-HCl is added to the superheater exit stream), can result in accelerated corrosion of the superheater vessels.

Figures 12 through 16 presented in this section were adapted from: A. C. Crawford, *Cost saving of using a metallurgical grade silicon with higher trichlorosilane yield in the hydrochlorination based polysilicon process*, Silicon for the Chemical Industry XIII, Nygård, Pachaly, Page, Rong, Tangstad, Tveit Eds., (Kristiansand, Norway), 2016, pp. 201-217.

Figure 16. Block flow diagram of the most common industrial Hydrochlorination process unit used in current (late 2024) large capacity TCS-based Siemens polysilicon plants. The green highlighted equipment show use of Incoloy 800H based directly on original Union Carbide corrosion studies with the system H_2 – STC – MGSi (these are the reactants fed to the HC reactor). The magenta highlighted equipment shows use of Incoloy 800H in a similar system as the HC reactor. The red highlighted area shows use of Incoloy 800H for the H_2 – STC system which is not supported by any corrosion studies. The red-orange highlighted area shows the use of Incoloy 800H for the H_2 – STC – HCl system which is not supported by any published corrosion studies. The gray sections do not use Incoloy 800H.



There are unconfirmed reports that some recently built HC units in China have deviated from use of Incoloy 800H as material of construction for the HC fluid bed reactor vessels and associated feed and off-gas piping. One material reported to be used is Haynes Alloy HR-120 UNS N08120). HR-120 is similar to Incoloy 800H. There are no known published corrosion studies relevant for HR-120 such as H_2 – STC – MGSi; H_2 – STC or H_2 – STC – HCl nor are there any reports about industrial experience with HR-120 use.

Another material that has been reported to be have been used is 347 Stainless steel (UNS S34700). East Hope (Xinjiang, China) is believed to have installed at least one HC FBR fabricated from 347SS in an effort to save CAPEX. The reactor was built by SunPower Group (See: https://en.sunpowergroup.com.cn). The reactor is reported to have "failed" in less than 3 years of operation. East Hope also experienced a significant process safety event on 17-June-2022 attributed to failure of a superheater. The superheater and associated piping is believed to have also been constructed of 347SS. A picture from this incident is provided in Figure 17.

Figure 17: Picture taken during 17-June-2022 East Hope (Xinjiang, China) process safety incident attributed to a superheated failure. See: https://www.bernreuter.com/newsroom/polysilicon-news/article/fire-halts-polysilicon-production-at-east-hope-for-one-month/ .

The leakage of a superheater caused a fire at East Hope's polysilicon plant in Xinjiang on June 17 – Screenshot: Bernreuter Research

Two corrosion study reports have been published in recent years. These followed the experimental protocol established in the late 1970's by Union Carbide. The selected materials for evaluation were "interesting" and not relevant to industrial HC operation: pure iron and 316L Stainless steel (UNS S31603). The work was done at Montana State University (Bozeman, Montana, USA). GT Advanced Materials (now Advanced Material Solutions [AMS] based in Missoula, Montana, USA) sponsored the 316L SS work. GTAT /

AMS is the leading supplier of complete turn-key TCS-based solar grade polysilicon technology where TCS is produced by the HC reaction. Perhaps AMS is in possession of unpublished, relevant corrosion data?

The iron corrosion study can be found here: Aller, Josh & Swain, Nolan & Baber, Michael & Tatar, Greg & Jacobson, Nathan & Gannon, Paul. (2017). Influence of silicon on high-temperature (600°C) chlorosilane interactions with iron. Solar Energy Materials and Solar Cells. 160. 410-417. 10.1016/j.solmat.2016.11.002. The 316L SS corrosion study can be found here: Josh Aller et al 2016 J. Electrochem. Soc. 163 C45.

J. Materials of construction conclusions

Some conclusions about materials of construction used in fabrication of industrial HC reactors (and other internals) along with the superheated sections of feed gas piping and equipment and the HC reactor off-gas piping and heat exchangers are presented to summarize this long section.

1) Continuous successful industrial HC operations starting in 1985 by Union Carbide / Advanced Silicon Materials (ASiMI) / REC Silicon in Moses Lake, Washington, USA and Butte, Montana, USA confirm the original selection of Incoloy 800H as a suitable material of construction for the HC reactor, upstream superheated gas feed and HC reactor off-gas piping.

2) Union Carbide's selection of Incoloy 800H was focused on the HC fluid bed reactor vessel. The selection was based on several corrosion studies combined with input from materials and vessel experts.

3) Union Carbide specification of Incoloy 800H on the superheated gas feed to the HC reactor, superheaters, reactor off-gas piping and associated cross heat exchangers was not based on direct corrosion results.

4) The Union Carbide / ASiMI / REC Silicon overall success with use of Incoloy 800H has required significant, never-ending "behind the scenes" work in the areas of a rigorous mechanical integrity program (routine external thickness measurements and internal visual inspections) and development of detailed operations, maintenance and return to service procedures. Without these support functions, the chances of long-term safe operation of this section of the industrial HC units cannot be guaranteed. An important "behind the scenes" area is identification and use of highly experienced Incoloy 800H vessel and piping fabricators who understand the nuances of Incoloy 800H.

5) The Union Carbide / ASiMI / REC Silicon overall success is based on operation within a constant and narrow set of boundary conditions that include no use of anhydrous HCl (A-HCl) co-feed and separation of H_2 and STC superheaters.

6) Safe operation of the large industrial HC units that are integrated with TCS-based polysilicon plants that include A-HCl co-feed, combination of H_2 and STC superheaters and use of alternate materials such as HR-120 is certainly possible but requires the "complete" Union Carbide / ASiMI / REC approach that has been described.

7) One missing area of supporting data are an expansion of published Incoloy 800H (and possibly related materials such as HR-120) corrosion data.

Make-up Chlorine

A TCS-based or silane (SiH_4)-based polysilicon plant that uses the hydrochlorination (HC) (Si + $2H_2 + 3SiCl_4 = 4HSiCl_3$) reaction to produce crude trichlorosilane (TCS; $HSiCl_3$) requires one or more sources of make-up chlorine. Ideally, there would be zero chlorine losses but industrial polysilicon production is far from ideal. There must be one or more sources of "make-up" chlorine to account for the total losses. There is a chance that the type of make-up chlorine used by OCIM and the way in which this make-up chlorine was added back to the overall plant contributed, but was not a root cause, to the fatal August 2024 accident.

Chlorine is lost in several areas of a HC-based polysilicon (TCS-based like OCIM or silane-based like REC, GCL) plant. It should be noted that molecular chlorine, Cl_2 (green gas), is not present in any polysilicon plant. The main chlorine losses are:

1) Metal chlorides ($AlCl_3$, $CaCl_2$, etc.). Some metallic impurities such as Aluminum (Al) and Calcium (Ca) present in the metallurgical grade silicon (MG-Si) consumed in the HC reactor to produce TCS are converted to chlorides. These metal chlorides leave the plant as unrecoverable solid wastes.

2) Slurry. Very fine solids that exit the HC fluid bed reactor and cyclone are captured by a scrubber. These solids exit the scrubber as a slurry (combination of fine solids, metal chlorides and chlorosilanes such as silicon tetrachloride [STC; $SiCl_4$]). The slurry is processed to recover most, but not all of the chlorosilanes while neutralizing the solids and remaining chlorosilanes. The neutralized chlorosilanes represent lost chlorine.

3) Vents. There are various process vent streams from all parts of the operations that include chlorosilanes such as TCS and STC. These vent streams are treated in scrubbers and any chlorosilanes present are "lost" as hydrochloric acid which is then neutralized in the main plant waste water treatment facility.

4) Purity purges. Purification of crude TCS produced in the HC unit to ultra-pure TCS suitable to produce solar grade polysilicon (9N or 10N for use in making n-type monocrystalline solar ingots) may require the intentional scrapping of small amounts of TCS and STC within the overall TCS purification section of the plant. These "purge" streams contain volatile carbon and phosphorus compounds. These purge streams are intentionally neutralized.

Historically, the source of make-up chlorine entering a polysilicon (TCS-based or silane-based) plant using HC as the route to crude TCS synthesis was STC. The STC was purchased from suitable external suppliers. STC was a "natural" source of make-up chlorine since STC is already one of the main feeds to the HC reactor. At times, instead of purchasing pure STC, a mixture of TCS and STC was purchased.

When the HC TCS synthesis route began to be used in the large TCS-based polysilicon plants that began operation in the late 2000's, the form of makeup chlorine began to change. Any TCS-based polysilicon plant generates a stream of anhydrous HCl (A-HCl) from the overall off-gas recovery (OGR) section of the plant. The OGR receives the combined off-gas streams from the individual TCS-based Siemens polysilicon reactors. This off-gas stream contains unreacted TCS, unreacted H_2, by-product STC, by-product A-HCl and other chlorosilane by-products.

For the legacy TCS-based polysilicon producers that use direct chlorination (DC) ($Si + 3HCl \rightarrow HSiCl_3 + H_2$) as the main route to production of crude TCS, the A-HCl recovered from the OGR is simply recycled back to the DC reactors where it is combined with other sources of A-HCl. The only source of make-up chlorine for producers running the DC process is A-HCl.

The HC process, as developed by Union Carbide for use in the silane (SiH_4) process, did not generate any stream of A-HCl. As HC became the predominate route to produce TCS for TCS-based polysilicon plants, there were three options for handling the A-HCl recovered in the OGR:

1) <u>Option-1 Scrap</u> – this was an option but not viable as scrapping the A-HCl stream recovered from the OGR would represent an unacceptable addition to the overall plant OPEX.

2) <u>Option-2 Feed to DC TCS synthesis unit</u> – build a DC TCS synthesis unit to consume the A-HCl from the OGR. The product stream of this unit, a mixture of TCS and STC, would then be fed to the main HC-based part of the plant. This method was practiced in the early days of using HC as the main route to TCS in TCS-based polysilicon plants. This option maintained the original Union Carbide HC design basis of not using A-HCl. This option resulted in increased plant CAPEX and OPEX since a DC TCS unit was required. The original Malaysia site technology provider selected by Tokuyama used this method at least in their original technology package.

3) <u>Option-3 Co-feed A-HCl to the HC Reactor</u> – Mix the A-HCl recovered from the OGR with the normal feed of H_2 and STC to the HC reactor. Option-3 became the only way to handle H-HCl recovered from the OGR by the early 2010's. This option, while not supported by any published HC work from Union Carbide or other industrial HC operators (notably published work on corrosion or process safety), represented the optimum method to handle OGR A-HCl in terms of CAPEX and OPEX. Inclusion of the A-HCl OGR stream resulted in a slight improvement in the overall heat balance on the HC reactor as the Si + HCl reaction is exothermic. Experience shows that the high operating temperatures of the HC reactor (~550^{o}C) resulted in no "gain" in TCS yield. High temperature in the Si + HCl reaction favors STC production over TCS production ($Si + 4HCl \rightarrow SiCl_4 + H_2$ and $HSiCl_3 + HCl \rightarrow SiCl_4 + H_2$).

TCS-based polysilicon producers using HC as the route to TCS production and co-feed of A-HCl with H_2 and STC continued to use purchased STC as the source of make-up chlorine originally. STC used for make-up chlorine typically was supplied by merchant TCS producers who produced TCS by DC for use in production of organofunctional silanes. As demand for TCS-based solar polysilicon increased, the supply of low-cost STC from the merchant TCS producers could not keep up. Some TCS-based solar polysilicon producers restarted old DC TCS units for the sole purpose of producing a mixture of TCS and STC for use as makeup chlorine to the larger HC units. Eventually, some of these polysilicon producers decided to by-pass the DC TCS route and explore the use of A-HCl as the source of make-up chlorine instead of STC or TCS / STC mixtures. The DC TCS units already required a source of A-HCl.

There are unconfirmed rumors that at least one Chinese HC technology provider is recommending use of molecular chlorine, Cl_2, as make-up chlorine. The reaction of Cl_2 and ground MG-Si powder is highly exothermic. Discussions with those who have run / attempted to run this reaction in a lab-scale reactor note the reaction is extremely violent. Use of Cl_2 as make-up chlorine for industrial HC-based TCS-based polysilicon plants cannot be recommended.

Currently (late 2024) it is believed that the large TCS-based solar grade polysilicon producers with TCS synthesis by HC are using various combinations of A-HCl, pure STC and TCS / STC mixtures as the sources of make-up chlorine to their HC units. Some may use both A-HCl (generated on-site or from a fence-line Chlor-alkali unit) and STC (or TCS /STC mixtures) and some may only use A-HCl.

In the cases where A-HCl is used as the make-up chlorine source, this stream of A-HCl is combined with the A-HCl stream recovered from the OGR section of the plant. When the make-up chlorine is 100% A-HCl or even a portion of A-HCl, the overall HC reaction moves from slightly endothermic to slightly exothermic. This is viewed by some producers as an advantage as higher HC reaction temperatures favor higher TCS yield but the true benefit is likely clouded by the fact that if the higher temperatures come from feeding more A-HCl to the HC reactor, the undesired parallel STC producing reactions are occurring (Si + 4HCl ✍ $SiCl_4$ + H_2; $HSiCl_3$ + HCl ✍ $SiCl_4$ + H_2).

The entry point of A-HCl to the HC reactor now becomes an interesting discussion. The discussion is the same if the only A-HCl being handled is from the OGR or if the A-HCl is from the OGR and the only source of make-up chlorine. There are two main ways to introduce the A-HCl to the HC FBR.

The most common A-HCl feed method is to combine the A-HCl with the combined stream of superheated H_2 and STC just before the main gas line enters the HC FBR. With this design, H_2 and STC superheating can be accomplished with separate superheaters (one for H_2, one for STC) or with a combined superheater (receives a mixture of H_2 and STC). The A-HCl is added after the superheater(s) and the combined stream of H_2, STC and A-HCl is fed to the bottom of the HC FBR. Figure 18 provides a block flow diagram of a HC process unit where the A-HCl is mixed with the main H_2 and STC feed.

An alternate A-HCl feed method is to mix the A-HCl with H_2 and feed the mixture of H_2 and HCl into the HC FBR reaction mass above the grid plate through an appropriately designed feed system. Figure 19 provides a block flow diagram of a HC process unit where the HCl is added directly to the HC FBR reaction mass.

Figure 18 and Figure 19 were adapted from: A. C. Crawford, *Cost saving of using a metallurgical grade silicon with higher trichlorosilane yield in the hydrochlorination based polysilicon process*, Silicon for the Chemical Industry XIII, Nygård, Pachaly, Page, Rong, Tangstad, Tveit Eds., (Kristiansand, Norway), 2016, pp. 201-217.

Figure 18: HC process unit where A-HCl recovered from the OGR and A-HCl used as make-up chlorine is mixed with the main superheated H_2 and STC stream just before entry into the HC FBR. Note the optional use of STC as source of some make-up chlorine.

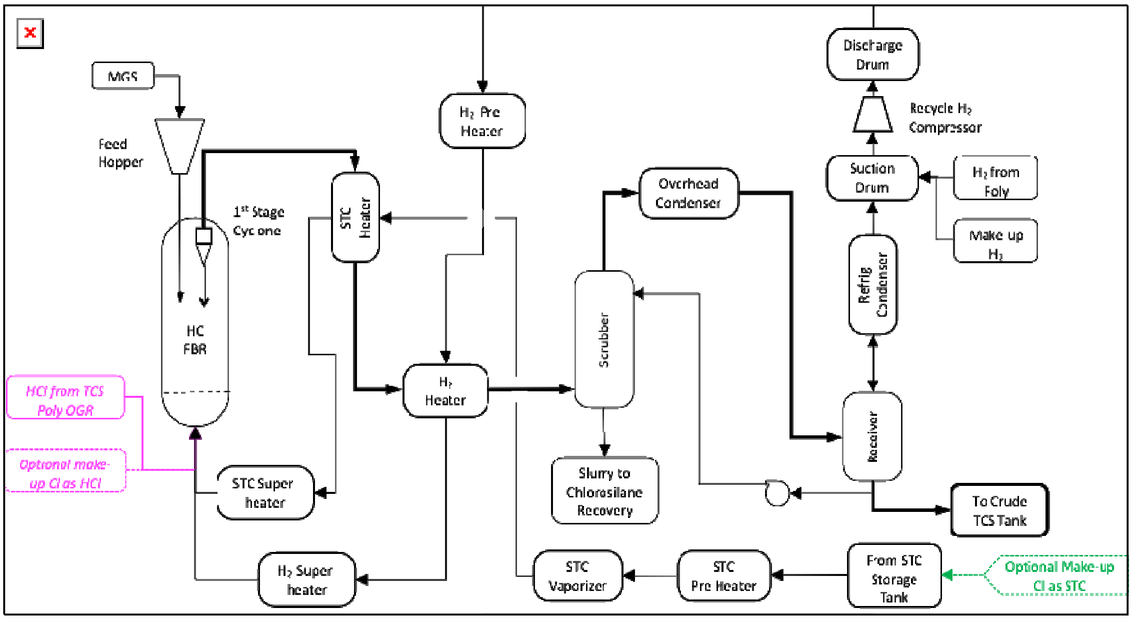
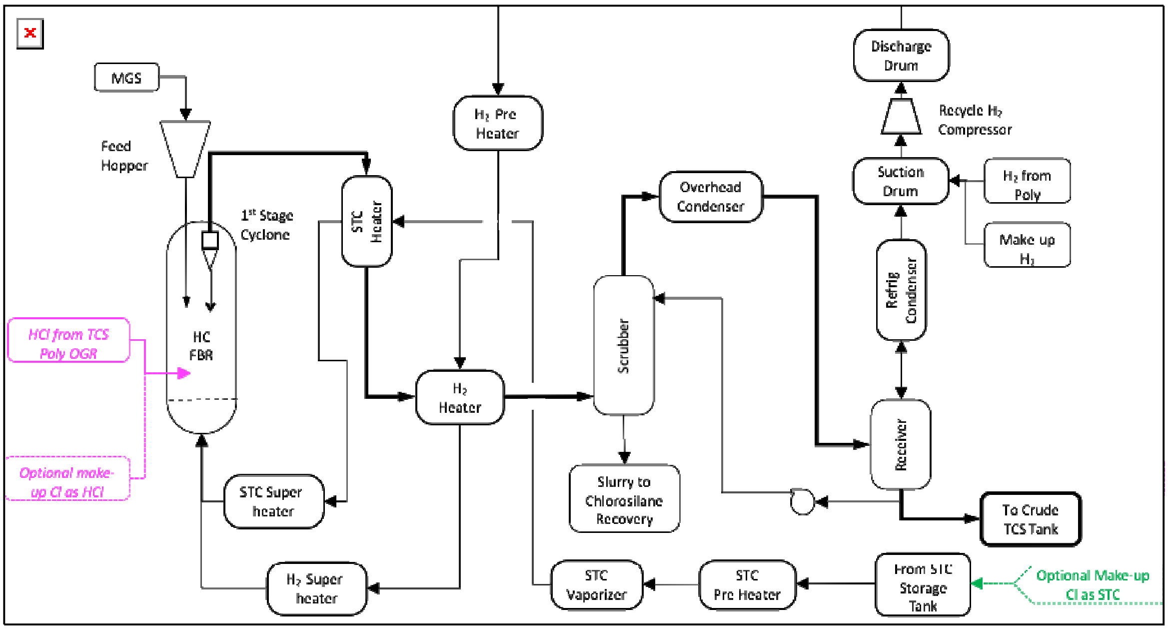


Figure 19: HC process unit where A-HCl recovered from the OGR and A-HCl used as make-up chlorine is added directly to the HC FBR reaction mass. Usually some H_2 is blended with the A-HCl stream. Note the optional use of STC as source of some make-up chlorine.



Operation of the HC process with any amount of A-HCl feed represents a departure from the original Union Carbide HC process design that has been in continuous operation since the mid 1980’s. A-HCl use in the HC process introduces new process safety risks. These risks have not been discussed nor quantified in any known publication. There are two areas of risk:

1) <u>Localized hot spots</u>

The reaction of ground MG-Si and A-HCl is well known in some parts of the silicon chemistry industry to be extremely exothermic. Reaction temperatures can easily exceed 1000^{o}C if the process is not designed to control the reaction temperature or to accommodate process upsets. At least one legacy producer of TCS via the DC route suffered a significant process safety incident in 1987 when a DC reactor was mistakenly run below minimum fluidizing velocity. Localized hot spots near the wall of the FBR resulted in the carbon steel FBR vessel failing due to a hole being melted in the side of the reactor. Luckily there were no injuries but there was a large release of HCl.

Both methods of A-HCl co-feed to the HC reactor can result in localized hot spots and temperatures exceeding 1000^{o}C. The more common method of adding the A-HCl to the main H_2 and STC streams (Figure 18) presents a higher risk of localized hot spots. This is because normal FBR operation results in some amount of MG-Si fines "sifting" through the grid plate holes and accumulating in the bottom of the FBR below the grid plate. Depending on the amount of MG-Si accumulated in the bottom of the FBR, the chance exists for A-HCl present in the main gas feed to react with the accumulated MG-Si and produce hot spots.

The hot spot risk from reaction of accumulated MG-Si under the grid plate can be eliminated by use of the alternate method of A-HCl feed (Figure 19). The alternate method requires initiation of A-HCl feed once the reaction mass is properly fluidized and requires stopping A-HCl feed before the reaction mass de-gasses during a normal shutdown.

Both A-HCl feed methods can result in localized hot spots if the wrong sequence is used to start and stop A-HCl feed to the reactor during normal operations and, more importantly, during reactor restart following an upset condition. Both A-HCl feed methods can be safely operated provided all risks are identified and the overall control system is properly designed.

The method of A-HCl co-feed used by OCIM is not known nor are details about the manner in which OCIM controls A-HCl feed.

2) <u>Increased corrosion</u>

High temperature A-HCl represents a significant corrosion challenge in any TCS synthesis process unit. There are no identified published corrosion studies showing the effect of A-HCl co-feed on the corrosion of the most popular material of construction used in HC FBR vessel construction and associated superheated feed gas piping, Incoloy 800H (UNS N08810). Corrosion data for the systems A-HCl – H_2 – STC – MG-Si and A-HCl – H_2 – STC are not available in the public domain. Some companies may have access to unpublished corrosion studies for these two systems that show Incoloy 800H is suitable. Otherwise, A-HCl co-feed, especially for the most common feed method (mixture with main H_2 and STC feed; Figure 11), is unsupported by corrosion data. Industrial HC operation with A-HCl co-feed can be viewed as on-going, full-scale corrosion studies.

The possible elevated corrosion rate of Incoloy 800H from A-HCl co-feed can be safely managed by implementation of a rigorous mechanical integrity program by the polysilicon producer combined with very detailed procedures, especially return to service procedures. There is no information available about how these programs and procedures at OCIM.

Ground Metallurgical Graden Silicon (MGS) Particle Size Distribution (PSD)
MGS is usually considered the key raw material used to produce trichlorosilane (TCS; HSiCl3) from the hydrochlorination (HC) ($Si + 2H_2 + 3SiCl_4 = 4HSiCl_3$) reaction. MGS is produced by the carbothermic reduction of silica (SiO_2) in submerged arc electric furnaces. The overall reaction is $SiO_2 + C$ ✍ $Si + 2CO$; where CO burns at the top of the open furnace to produce CO_2: $CO + ½O_2$ ✍ CO_2. Silica (SiO_2) is quartz rock or gravel mined from the Earth. The carbon reductant is primarily metallurgical grade coal and / or charcoal; most Chinese MGS producers also use petroleum coke as a carbon reductant. Wood chips are also fed to the furnace and help with efficiency of the very complex chemical reactions.

Molten MGS is periodically removed (tapping) from the furnace and into ladles. The molten silicon is refined by addition of oxygen into the ladle to achieve desired levels of Aluminum (Al) and Calcium (Ca). All other impurities present in the final MGS product, including Arsenic (As), Boron (B), Chromium (Cr), Iron (Fe), Magnesium (Mg), Manganese (Mn), Nickel (Ni), Phosphorus (P), Lead (Pb), Titanium (Ti) and Vanadium (V), are controlled by selection of raw materials added to the furnace. Each HC-based TCS producer has a specification for all impurities.

The refined molten silicon is poured (Casting) into large molds where it solidifies into large rectangular ingots (about 1 m x 1 m x 100 mm). The solidified ingots are crushed into lumps (most common lump size is 10 mm x 100 mm) and the lump MGS is packaged for shipment to the customer.

TCS synthesis by Hydrochlorination (or Direct chlorination) requires use of ground MGS powder. Almost all polysilicon producers that synthesis TCS by HC (TCS-based and silane-based) do not operate lump MGS grinders. These companies purchase ground MGS powder from a wide range of either independent grinders or, in some cases, the MGS smelter operates a grinder. The particle size distribution (PSD) of the ground MGS powder is a very important parameter and should be tightly controlled by the lump MGS grinder.

Design of the HC fluid bed reactor and internal first stage cyclone (if used) is based on use of a very specific ground MGS PSD. Once the HC FBR and cyclone have been designed, changing the ground MGS PSD can be a very involved process as changes to the FBR and cyclone maybe required. The PSD for most ground MGS used in industrial HC reactors has a median (d50) particle size of about 150 – 180 microns (some producers may use PSD with a much higher media size). The “fines” content of ground MGS used in almost all industrial HC reactors is low. Fines are defined as particles smaller than at least 75 microns if not 54 microns or 44 microns. The normal specification limit for fines content in ground MGS powder is in the range of 2 to 3 weight % maximum.

If ground MGS with a significantly different PSD than used in FBR design is used in an industrial HC reactor, significant operational problems may be experienced especially if the altered PSD contains a much higher content of fines. Higher fines content can result in significantly higher entrainment of fines from the HC reactor and first stage cyclone. This can result in problems with operation of the downstream solids scrubber. Higher fines content can also result in problems with efficient operation of the gas distributor located at the bottom of the HC FBR. Excess fines can result in excessive pressure drop across the grid due to a higher rate of individual grid holes becoming plugged. The amount of fine MGS that "sifts" through the grid holes and enters the area under the grid plate, which usually contains a very small amount of MGS fines when the correct ground MGS PSD is used.

Problems with ground MGS PSD that is significantly different than the PSD used to design the HC FBR and cyclone can be the result of two very different scenarios. The most common problem resulting in a large deviation of the ground MGS PSD is related to how the lump MGS grinder (or grinders as is usually the case) monitor and control the grinding process. There are many variables that impact final PSD in a lump MGS grinding plant and if the grinding plant operator is not diligent, the variation in PSD can be very high. The polysilicon producer must maintain very close relationships with all lump MGS grinders to ensure close adherence to the required PSD specifications.

Since almost all industrial HC operators do not operate their own lump MGS grinding plant, ground MGS powder is usually supplied by multiple grinders. Each grinder can have a different PSD and the ground MGS PSD specifications are normally broad enough to enable use of these different PSD's. Given the importance to operate with very tight ground MGS PSD, the global silicone industry (MGS is used to synthesize methylchlorosilanes) long ago realized that self-grinding of purchased lump MGS was a best practice.

The second scenario that can result in significant deviation from the PSD required by HC FBR and cyclone design is intentional modification of the PSD spec by the HC plant operator. Intentional modifications are frequently done (commonly driven by the purchasing group) without understanding the possible effect on HC FBR operation.

The normal ground MGS PSD specification has a very low maximum level of total fines content. As previously noted, this is normally in the range of 2 – 3 weight % maximum content of 75 micron and smaller fines. When lump MGS is ground, the "raw" fines content can range from 8-10 weight percent to greater than 30 weight % depending on the type of mill used. To achieve the desired maximum allowable fines content, the lump MGS grinder must remove the excess fines present in the "raw" ground MGS normally by screening.

These removed grinding "fines" represent a significant overall silicon yield loss. The value of MGS normally decreases as the physical size decreases. Finer MGS has fewer commercial applications. MGS lump that is 100 mm can be used in almost any application (provided the impurity content is "correct") while MGS fines with top size of 75 microns has very limited industrial applications. Historically, the value of MGS fines is 40 – 60% the value of lump MGS.

While the polysilicon producer may be only purchasing ground MGS that meets their desired PSD specification, in actuality, the producer is really purchasing lump MGS. Their delivered cost of ground MGS at the correct PSD is comprised of the lump MGS price, the lump MGS grinding cost and, most importantly, the cost incurred by the lump MGS grinder to remove and "dispose" of the MGS fines that are not included in the final ground MGS product. This grinding "fines loss" can add substantial cost to the overall delivered price of ground MGS powder to the polysilicon plant. In many cases, the polysilicon producer may not be fully aware of this incremental cost. The grinding “Fines loss” has a direct impact on the total OPEX of the polysilicon producer.

Some polysilicon producers fully understand the impact of grinding “fines loss” on their OPEX. These producers can be tempted to relax the ground MGS PSD specification to enable receipt of ground MGS with a significantly higher “fines” content. The fines content could increase from the standard 2 – 3 weight % maximum to anywhere from 10 to 30% maximum. The delivered cost of the higher fines content MGS is lower as the required grinding “fines loss” is much lower.

The use of higher fines content ground MGS can be a significant “positive” to overall polysilicon plant operations through significant OPEX reduction. However, if such a PSD change is not properly implemented, significant operational, maintenance and even process safety problems can be experienced. A well-run project with the goal of using higher fines content ground MGS must include an initial detailed evaluation of the current HC FBR and cyclone design followed by implementation of necessary modifications to equipment such as the FBR grid plate and / or the first stage cyclone.

OCIM Fatal 14-August-2024 Hydrochlorination Accident Analysis

Identification and Analysis of Potential Failure Modes

Analysis was provided in an earlier section of the document to show, with a high degree of confidence, that the accident occurred in the following location:

1) The August 2024 accident occurred in a HC process unit.

2) The August 2024 accident occurred in the bottom area of the HC reactor process tower which is the central part of an overall HC process unit.

3) The accident occurred in one of the four HC process units originally built by Tokuyama as Phase-2 of the site.

The analysis combined photographs and video of the accident with experience of the author in design and operation of industrial trichlorosilane (TCS; HSiCl3)-based polysilicon plants with TCS produced by the Hydrochlorination (HC) reaction ($Si + 2H_2 + 3SiCl_4 = 4HSiCl_3$).

This section of the document provides a list of potential equipment that could have failed. Analysis will be provided as to how each piece of equipment could fail, known historical failures of the same equipment and comments on the likelihood that OCIM August 2024 was a result of the specific equipment failure.

Potential OCIM August 2024 Failed Equipment
This section is prepared based on 20-year first-hand experience with design, operation and maintenance of industry Hydrochlorination (HC)($Si + 2H_2 + 3SiCl_4 = 4HSiCl_3$) process units. OCIM has not released any information about the exact failure from the August 2024 fatal accident.

The following specific process features located at the bottom of the HC fluid bed reactor (FBR) may have failed in the OCIM August 2024 fatal accident.

1) Main gas feed line between H_2 and STC superheater discharges and connection to the HC FBR.

2) HC FBR vessel wall in the location adjacent to where the grid plate is attached.

3) Anhydrous HCl (A-HCl) feed line. There are two possible A-HCl feed pipe locations. Figure 20 shows addition to the main gas feed line; Figure 21 shows addition into the reaction mass above the grid plate.

4) HC FBR vessel nozzle. There are several nozzles located in the bottom area of the reactor. These include a manway on the bottom head, a manway on just above the grid plate and a nozzle used to remove the spent reaction mass.

Figure 20 and Figure 21 highlight the four possible failure areas listed above. Figure 20 assumes anhydrous HCl is added to the main gas feed line; Figure 21 assumes A-HCl is injected into the reaction mass above the grid plate. The actual OCIM A-HCl co-feed configuration is not known. Figure 20 is an enlargement of Figure 18 showing just the area associated with bottom of the HC reactor. Figure 21 is an enlargement of Figure 19 showing just the area associated with bottom of the HC reactor.

Figure 20: HC process unit with the four potential OCIM August 2024 fatal accident failure locations identified. Anhydrous HCl co-feed is mixed with main gas feed.

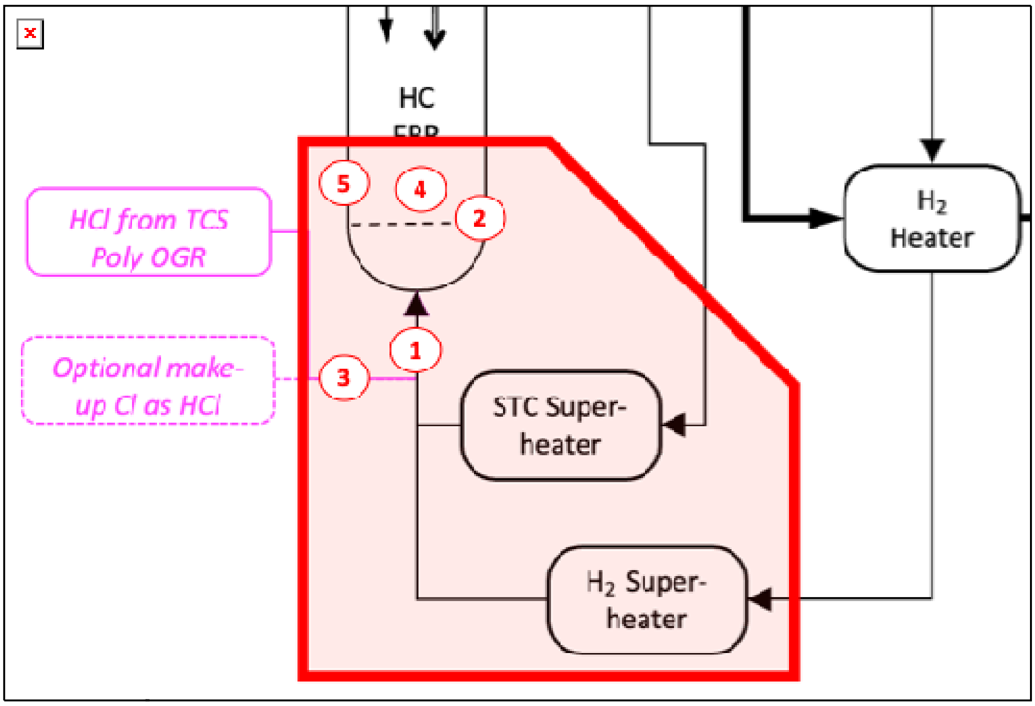


Figure 21: HC process unit with the four potential OCIM August 2024 fatal accident failure locations identified. Anhydrous HCl co-feed is injected into the reaction mass above the grid plate.

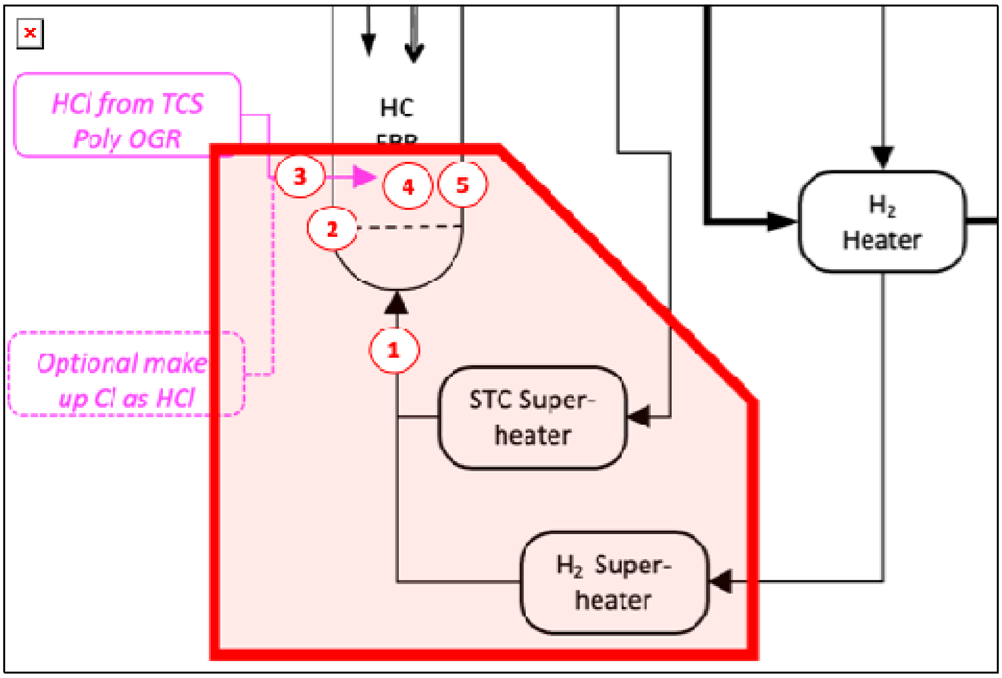


Table 1 provides a list of potential causes of each of the four identified failure locations. Table 1 assumes that the correct materials of construction were used for the process piping and HC fluid bed reactor vessel. This is a good assumption based on direct experience with the original technology provider to the Malaysia site (Company A) with regards to HC technology provided to KAM (Korea Advanced Materials). Company A HC technology supplied to KAM required use of Incoloy 800H (UNS N08810).

Not listed on Table 1, but applicable to each of the failure locations, is OCIM not following a rigorous mechanical integrity (MI) inspection program (internal and external) or OCIM not developing and always following detailed procedures associated with startup, shutdown, maintenance preparation and return to service (aka “standard operating procedures” or SOP’s). An industrial HC unit designed, operated and maintained to world class engineering standards could still experience a catastrophic failure similar to the OCIM August 2024 accident if rigorous MI and SOP’s are not developed and always followed.

Table 1: Potential OCIM August 2024 fatal accident failure locations and potential causes of each failure.

Failure Location	**Potential Failure Causes**			
1) Main gas feed pipe	Internal corrosion	Internal erosion	Failure to follow best practices for Incoloy 800H piping fabrication	Excess thermal pipe stress
2) FBR vessel wall @ grid attachment	Wrong grid attachment mechanical design			
3) Anhydrous HCl co-feed pipe	Internal corrosion	Internal erosion	Failure to follow best practices for Incoloy 800H piping fabrication	Excess thermal pipe stress
4) FBR vessel welds	Failure to follow best practices for Incoloy 800H vessel fabrication			
5) FBR vessel nozzles	Failure to follow best practices for Incoloy 800H vessel fabrication	Internal corrosion	Internal erosion	

The H_2 and STC superheaters are located close to the bottom of industrial HC fluid bed reactors. The reason for the close location is to minimize heat loss from the exit of the superheaters to the HC FBR feed. While the H_2 or STC superheater could have been the location of the OCIM August 2024 accident failure, the superheaters are eliminated based on visual evidence of the accident.

The color of the “cloud” associated with the OCIM August 2024 accident is dark gray near the source (bottom area). The color of the “cloud” associated with a June 2022 accident that occurred at East Hope Polysilicon (Xinjiang, China) attributed to a superheater failure is not as dark. The dark cloud from the OCIM August 2024 accident suggests the failure occurred close to the HC FBR which enabled immediate release of the HC FBR contents, which includes a high inventory of “reaction mass” (partially reacted ground MG-Si powder). Reaction mass is dark gray in color. If the OCIM August 2024 failure had occurred at one of the superheaters (H_2 or STC), the color of the cloud would be lighter but not white (see Figure 5; Wacker chlorosilane only release). Figure 22 compares cloud colors from OCIM August 2024 and East Hope June 2022.

Figure 22: Comparison of cloud color from the OCIM August 2024 unspecified accident (image taken from Figure 4) and the East Hope June 2022 accident attributed to a superheater failure (image taken from Figure 17). The OCIM cloud is darker than the East Hope cloud.

Analysis - Main Gas Feed Pipe Failure
Failure of the main gas feed line to the hydrochlorination (HC) ($Si + 2H_2 + 3SiCl_4 = 4HSiCl_3$) fluid bed reactor (FBR) could easily result in the fatal accident experienced by OCIM in August 2024. Figure 20 and Figure 21 show the location of this pipe.

An inherent process design problem related to the main gas feed line is the lack of an emergency isolation valve located on the nozzle of the HC FBR bottom head where the main gas feed line is attached. An emergency isolation valve could be closed should a catastrophic failure of the main gas feed line occur to prevent de-pressure / de-inventory of the HC FBR. The visual evidence from the OCIM August 2024 accident definitely point to HC FBR de-pressure / de-inventory to the atmosphere.

The high operating temperature (~525 – 575^{o}C) and high operating pressure (20 – 30 barg) combined with the chance to have some abrasive metallurgical grade silicon (MGS) present makes identification of a reliable on/off valve very difficult. The less severe operating conditions of the direct chlorination trichlorosilane synthesis FBR (Si + 3HCl; ~300^{o}C and ~2.8 barg) and the Rochow-Müller direct methylchlorosilane synthesis FBR (Si + CH_3Cl; ~300^{o}C and ~2.8 barg) enables use of emergency isolation valves where the main gas feed lines are connected. The OCIM HC unit involved in the accident may have had an emergency isolation valve but, if the failure was the main gas feed line, the valve did not close. Also unknown is the process design of the OCIM HC unit in terms of how to safely vent-down the HC FBR should a catastrophic failure occur.

A. Internal corrosion – Main Gas feed line

There is always internal corrosion of the main gas feed line regardless of whether the pipe only contains a mixture of superheated silicon tetrachloride (STC; $SiCl_4$) and hydrogen (H_2) or includes anhydrous hydrogen chloride (HCl) co-feed. The pipe does not contain MG-Si so "easy" formation of the protective nickel silicide ($NiSiCl_2$) coating (found in the HC FBR vessel which does contain MG-Si) does not occur.

Given the normal excess H_2 feed, the combined H_2 and STC system in the main gas feed line is in the HCl "etch" mode for the system: Si – H – Cl (see: L. P. Hunt and E. Sirtl 1972 *J. Electrochem. Soc.* **119** 1741). The short residence time of the combined gas feed line (at least in most industrial designs the combined gas feed pipe is very short) should limit internal corrosion. If OCIM operation includes anhydrous HCl co-feed with the H_2 and STC (see Figure 13), then there would be a greater rate of corrosion.

B. Internal erosion – Main Gas feed line

Through normal HC FBR operation, a small amount of MGS powder can be present below the HC grid plate. Even the most optimally designed and operated FBR will experience a small amount of fines "sifting" through the individual grid holes. The amount of sifting is a function of many variables including the design of the individual grid holes. First-hand experience with HC reactors using the original Union Carbide grid hole design shows a very low amount of fines "sifting" through a wide range of operating conditions (as noted above, no more than 50 kg, and usually less than 25 kg of MGS fines observed below the grid plate). Importantly, in all cases related to this first-hand experience, the only ground MGS consumed was that of low overall fines content.

Depending on the specific design of the HC FBR bottom head and details of how the main gas feed line is connected to the HC FBR bottom head nozzle, perhaps some MGS powder could migrate into the main gas feed line. The chances of MGS powder being present in the main gas feed line seem very low but could be possible.

MGS powder is very abrasive. If sufficient amounts of MGS powder enter the main gas feed line, a catastrophic failure from internal erosion of the pipe could happen and the time required would not be very long. When MGS powder is present in a location not designed to contain MGS powder and this MGS powder is contacted with high volume gas flow, localized rapid internal pipe erosion has been observed to occur.

How did MGS powder enter the area under the fluid bed reactor (FBR) grid plate and into the main gas feed line? Was this a one-time event or was there a chronic problem with the HC FBR design / operation that enabled sufficient MGS to enter the area under the grid plate and into the main gas feed pipe? Was OCIM even aware that MGS of sufficient amount to result in localized erosion had entered the area under the grid and into the main gas feed pipe?

These important questions are not easy to answer. Some questions required to answer these questions include details of mechanical design of the impacted OCIM HC FBR grid plate or individual holes on the grid plate. Process information such as ground MGS particle size distribution, operating conditions (total gas flow, temperature, pressure, bed level), operating procedures or *upset operations* would also need to be known.

Upset operations would include short-term process upsets, such as a power “blip”, that would result in loss of fluidizing gas flow to the HC FBR. While text book industrial FBR operation suggests anytime there is fluidization loss that the reaction mass be 100% removed from the FBR prior to restart, first-hand experience shows that this never happens. In fact, most (all?) industrial HC units do not contain a dedicated vessel designed to receive the contents of the FBR. The only way to empty these HC FBR’s is to scrap the entire reaction mass by dumping to an open bin or similar container.

In contrast, industrial methylchlorosilane (silicone precursors) and direct chlorination trichlorosilane (TCS; $HSiCl_3$; Si + 3HCl) FBR’s include a “spent bed hopper” that is designed to receive the reaction mass. A temporary shutdown resulting in loss of fluidization can be “easily” handled in these units by fast transfer of the reaction mass out of the FBR into the spent bed hopper; the FBR can then be restarted and the reaction mass transferred back to the vessel.

Most importantly, there are no data about any process design / operation changes made by OCI to the Malaysia plant since they purchased the site from Tokuyama. Any industrial HC process unit is designed to operate within a very narrow set of operating conditions.

Deviation from these design conditions has the chance to alter process operation. The altered process operation can result in transition from safe to unsafe conditions.

A possible change that OCIM made to plant operations that could result in transition from safe to unsafe operation (in terms of MGS entering the area under the grid at amounts higher than normal) is a change to the ground MGS PSD. The ground MGS used by most industrial HC unit operators intentionally contains a limited amount of "fines" where fines are defined as particles less than 75 microns or less than 54 microns.

Inclusion of fines in the ground MGS fed to the HC reactor reduces cost of the ground MGS. Removal of "fines" represents a significant yield loss due to the low value of fine silicon powders. Pressure to reduce plant OPEX may have forced OCIM to include a higher amount of MGS fines in the ground MGS. Higher fines content ground MGS, combined with a failure to recognize the potential impact of FBR operation with the higher fines content MGS, could result in more MGS fines entering the area under the grid plate and into the main gas feed pipe.

An alternate explanation of the inclusion of higher fines in the ground MGS is that OCIM began purchasing ground MGS from a new lump MGS grinder and this company failed to establish stable grinding operations and / or accurate quantification of the ground MGS PSD. A related cause is that an already qualified OCIM ground MGS supplier failed to accurately quantify the PSD of ground MGS delivered to OCIM. These possible problems would require detailed knowledge of OCIM's supplier qualification procedures.

C. Materials of Construction – Main gas feed line

It is assumed that the main gas feed line was constructed of Incoloy 800H (UNS N08810), which is regarded as the only proven material of construction for this application. There are recent (last 2-4 years) reports that some producers are using different materials than Incoloy 800H. The chances that materials other than Incoloy 800H were used when the Malaysia site was built by Tokuyama in the early 2010's are almost zero. There is no way to know if OCI replaced original Incoloy 800H piping with different materials; if this happened then this would definitely be viewed as a root cause of the accident. The current HC units operated by REC Silicon have experienced safe operation of the main gas feed line to the HC reactors starting in 1985 when the first HC unit started in Moses Lake, Washington, USA.

It should be noted that even with use of Incoloy 800H, there is no way to know the history of the specific section of pipe such as use of post weld heat treatment, design of mechanical supports to accommodate thermal expansion, procedures used to prepare the pipe for opening to the atmosphere and procedures used to return the pipe to service. These details, if known, could provide more clues about why the pipe failed. An improperly designed industrial Incoloy 800H piping system represents a high failure risk.

First-hand experience has shown that Incoloy 800H pipe welds can crack from stress relaxation or chloride stress corrosion. In these cases, the cracks were found in routine mechanical integrity inspections during planned HC unit shutdowns. If a crack were to occur and not be detected soon enough, the chance for a catastrophic failure occurring due to the crack and normal thermal stress associated with startup of the HC process unit (from ambient temperatures to temperatures greater than about 550°C is high. The failure risk increases if the piping system has not been designed to accommodate thermal expansion or if undocumented changes were made to the original, properly designed piping system.

D. Practices and Procedures – Main Gas feed line

When an industrial HC unit is operated by an experienced and competent company that has a rigorous mechanical integrity checking program along with strict standard maintenance, operating and return to service procedures, the internal corrosion of the main gas feed line is viewed as manageable with low risk of catastrophic failure. The company must also have a strict management of change program to identify proposed process changes that could result in unanticipated accelerated internal corrosion of the main gas feed line if implemented. First-hand experience points to REC Silicon as a best-in-class benchmark for competence in this area.

If the industrial HC unit operator fails to have the above mentioned practices and procedures in place and always followed, the risk of failure of the main gas feed line from normal (or abnormal due to process changes made without proper assessment) moves from low risk to high risk. This is assumed to be the root cause of the OCIM 14-August-2024 fatal accident.

Of special note is concern that OCIM failed to maintain and follow rigorous return to service procedures to ensure that the main gas feed line had been properly cleaned (to remove any internal scale or solids that will contain adsorbed chlorosilanes and provide a source of localized highly concentrated hydrochloric acid) and dried prior to the unit being restarted. The site is in a high humidity location which makes cleaning and drying extremely important.

Analysis – Hydrochlorination Fluid Bed Reactor Vessel Failure @ Grid Plate Attachment
The method of attachment of the grid plate to the Hydrochlorination (HC) ($Si + 2H_2 + 3SiCl_4 = 4HSiCl_3$) fluid bed reactor (FBR) represents a potential failure location that *could* result in an accident similar to that experienced by OCIM in August 2024. This potential failure mode in the bottom area of the HC FBR is dependent primarily on the mechanical design of the reactor vessel.

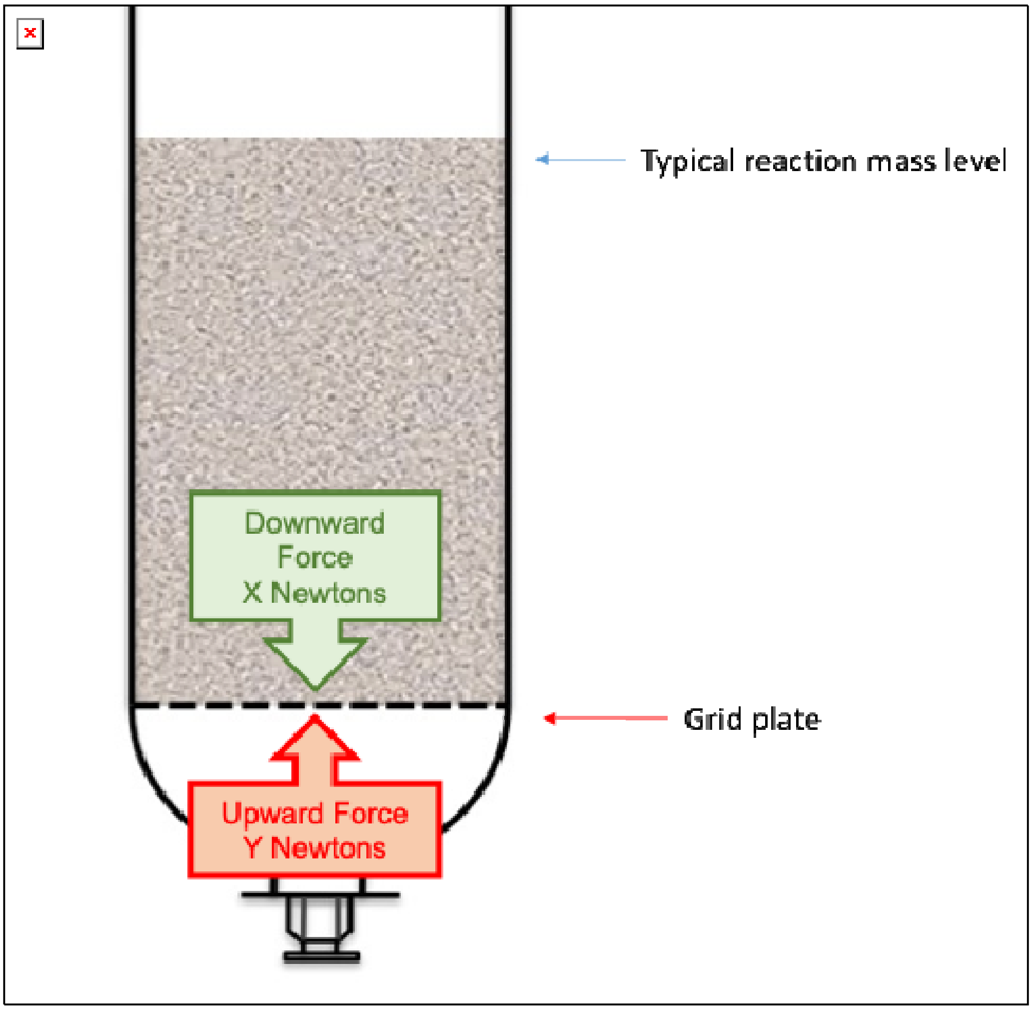
The specific method of how the grid plate is welded to the FBR vessel is critical. The attachment method must be designed to accommodate both downward and upward forces. The grid plate of any FBR must be attached to the FBR vessel. The attachment method can be dependent on the actual grid plate design (flat or conical) but not on the design and number of individual grid plate holes. The universal attachment method in modern HC FBR's is welding. The original Union Carbide HC FBR built in the early 1980's used a design where the grid plate was bolted to an internal flange (more about that later in this section). Detailed mechanical design of how the grid plate is welded to the HC vessel requires proper specification of design downward and upward forces subjected to the grid.

First-hand experience indicates establishment of an adequate design basis for the downward force is well understood. For an HC reactor, the design basis for downward force is generally the HC FBR with a "full inventory" of de-fluidized reaction mass. There are some nuances in how "full inventory" is defined. The problem arises with specification of the correct design basis for the upward force. Some industrial HC reactor designs prepared by large, global engineering firms have failed to recognize any upward force on the grid plate other than the normal operating pressure drop. The correct design upward force is usually based on the maximum discharge pressure achievable by the hydrogen recycle compressor combined with assuming gas flow through the grid plate holes is not possible.

The only attachment method to properly accommodate these downward and upward forces is for the grid plate to be ***strength welded*** to the HC FBR vessel around the circumference. Larger diameter HC FBR's with flat grid plates also use horizontal support beams located under the grid. The beams must be properly strength welded to the vessel. Proper designs for attachment of conical grid plates are more complicated.

A very common design flaw observed in many industrial HC reactors is improper design of the grid plate attachment. While most designs properly account for the downward force, the same is not true for the upward force. The resulting mechanical design is for a grid plate that is only seal welded to the vessel. When horizontal support beams are used for larger diameter reactors having flat grid plates, some proposed designs have not even included seal welding the grid to the support beams. If the grid plate is only seal welded to the vessel and perhaps just resting on the horizontal support beams, a serious HC vessel failure mode has been enabled. Figure 23 shows a typical HC FBR with combined downward and upward forces.

Figure 23: Typical HC FBR showing combined downward and upward forces that must be considered in the design of grid plate attachment to the HC vessel. The total downward force is usually based on “full inventory” of non-fluidized reaction mass. The total upward force is usually based on maximum discharge pressure that can be achieved by the recycle H_2 compressor. Specific values of the downward and upward forces are not provided; these are considered trade secrets.



A. <u>Grid Plate Seal Weld Failure Description</u>

Figure 24 shows a simplified HC vessel failure that is initiated by a mechanical design where the grid plate is only seal welded to the vessel. Figure 24 shows a flat grid plate; the HC vessel failure can also occur with a conical grid plate attached to the vessel by seal welding.

1) **Image A**: Normal HC FBR operation.

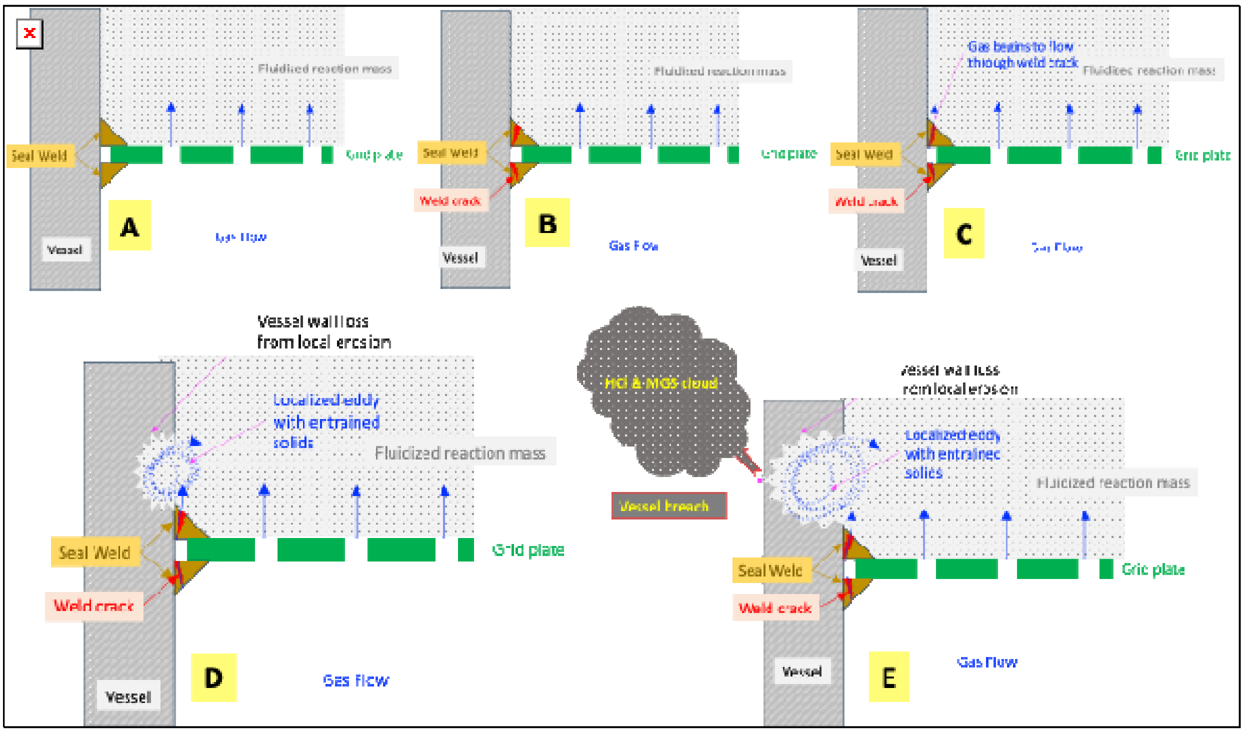
2) **Image B**: An unidentified operation upset (possible upsets to be discussed below) has occurred resulting in a portion of the seal weld cracking.

3) **Image C**: Flow of some fluidizing gas (superheated H_2, STC and optionally Anhydrous HCl depending on A-HCl feed configuration) through the cracked seal weld begins.

4) **Image D**: The flow of high velocity gas through the crack adjacent to the inside HC vessel wall entrains abrasive reaction mass (ground MGS) in localized "eddies". These "eddies" result in high velocity impingement of abrasive solids on the HC vessel wall which begins to erode away the wall.

5) **Image E**: The impingement of the combination of abrasive solids and high velocity gas has eroded a hole completely through the side of the HC vessel wall. The vessel breach begins as a "pin hole" but quickly increases in size due to the discharge of high pressure (20 – 30 barg) contents of the FBR into the atmosphere.

Figure 24: Progression of HC vessel failure due to use of mechanical design with grid plate attachment to the HC vessel by seal welding.



Until the vessel breach actually occurs, there is no early warning / indication of the pending failure. If the hole / leak is quickly discovered by operating personnel either by routine walk-through checks of the unit or remote monitoring via video cameras, a rapid but controlled shutdown of the HC unit should be possible (pressure reduction being the important activity) and the de-pressure / de-inventory of the HC FBR minimized. If the leak is not quickly detected, the size of the hole can quickly grow due to localized abrasion of the vessel wall by impingement of abrasive reaction mass. There is a chance to have an accident of the magnitude experienced by OCIM in August 2024.

B. <u>HC FBR Grid plate operation details</u>

When a FBR is operating properly (reaction mass is fluidized and gas distribution through the grid is normal), the differential pressure (DP) across the grid plate is about 20% of the differential pressure across the reaction mass. Some HC FBR's are provided with instrumentation to measure grid and reaction mass DP.

When a FBR is not operating properly, the grid DP can be very high. High / excess DP can result from having an excess number of individual grid holes (a large diameter HC FBR can easily have 100-200 individual holes with a unique hole design) that have become plugged or severely restricted. The worst case scenario is when all grid holes are temporarily blocked or severely restricted.

Plugged or restricted holes can result from many upset conditions but the most common is some type of HC process unit upset that results in temporary loss of fluidizing gas flow. This loss of gas flow results in loss of reaction mass fluidization. As time proceeds before gas flow is reestablished, the reaction de-gasses until, in a worst case, the reaction mass is completely degassed. A common upset resulting in loss of fluidizing gas flow is a power failure. While most power failures are very short-lived, experience shows that recovery of a large industrial HC unit can take an extended time for a variety of reasons. Some recovery problems include difficulty to restart hydrogen compressors and / or STC feed pumps.

C. <u>Known HC FBR vessel breach at Grid Attachment</u>

There are two known industrial HC FBR accidents that were caused by improper mechanical design of the grid attachment. Both of these accidents resulted in multiple breaches of the HC FBR vessel wall just above where the grid was attached. These two accidents were quickly discovered by operating personnel and the units were shutdown. As a result, the impact of the leaking contents of the HC FBR (H_2, STC, TCS and reaction mass) was minimized. A small cloud of HCl and burning reaction mass was observed. Due to the quick detection of these leaks, there were no injuries or off-site impact.

1) *Union Carbide; Moses Lake, Washington, USA*

The original industrial HC FBR was started by Union Carbide in 1985. The grid plate of this reactor was bolted to an internal flange welded to the inside of the HC FBR vessel. Soon after initial startup, portions of the gasket between the flange and grid plate was not properly sealed. This allowed by-pass of fluidizing gas through the non-sealed gasket areas and between the outside diameter of the grid plate and inside diameter / surface of the FBR vessel wall. While not a cracked seal weld, as described above, the action of high velocity gas leaking past the failed areas of the gasket and abrasive reaction mass resulted in the same localized erosive failure of the FBR vessel wall. The time between initial HC FBR startup and the FBR vessel wall leak was less than 7 days.

This failure was not caused by excessive upward force. Union Carbide repaired the vessel wall holes and then welded a "shroud" around the circumference of the grid plate. One edge of the shroud was welded to the top of the grid plate and the other edge was welded to the FBR vessel wall just above the grid. The purpose of the shroud was to provide a backup should the gasket on the internal grid plate mounting flange fail again. This HC unit safely ran until the entire bottom of the reactor was replaced in the late 1990's (due to identification of cracks in the main vessel circumferential welds).

All future HC FBR's built by Union Carbide / Advanced Silicon Materials (ASiMI) / REC Silicon in Moses Lake, Washington, USA; Butte, Montana, USA; and Yulin, Shaanxi, China (Joint venture) were designed with flat plate grids strength welded to the FBR vessel wall. There are no known problems with the grid attachment of these reactors.

2) *Korea Advanced Materials (KAM); Daejuk, South Korea*

KAM (joint venture between KCC and Hyundai) built a TCS-based Siemens polysilicon plant in Daejuk, South Korea (site of a KCC Silicones plant and a KCC Polysilicon plant that used the Ethyl Corporation fluorine route to silane). Plant construction started in 2008 and operation began in 2010. KAM purchased the turn-key TCS-based polysilicon technology from USA-based Company A. Some Company A employees had previously worked for Advanced Silicon Materials. KAM was one of the first customers of Company A. Company A also supplied the HC process technology to Tokuyama when the Malaysia site (now run by OCIM) was initially developed. The HC reactors built at KAM were the same diameter as the original Union Carbide Moses Lake HC reactors.

The author of this document was working for KCC Silicones when the KAM polysilicon plant began initial operation in May 2010. The first HC reactor experienced a vessel wall breach less than 72 hours after initial startup. The flat grid plate was only seal welded to the HC vessel wall. The seal weld cracked in several locations and the HC FBR vessel wall failed from localized high velocity gas jets with impingement of abrasive reaction mass (see Figure 24).

The failed reactor was repaired by the original fabrication shop and the second HC reactor, which has not been placed in operation, was modified. The repair / modification was to strength weld the grid plate to the HC FBR vessel wall. Once these modifications were made, the reactors did not experience additional operational problems for the life of the KAM plant.

KAM did share details of the failure and the corrective actions (strength welding the grid plate to the FBR vessel) to Company A. It is not known if Company A made changes to the mechanical design of their HC FBR to include strength welding the grid prior to selling HC technology to Tokuyama for the Malaysia site. As described earlier in this document, visual evidence of the OCIM August 2024 accident clearly indicates this fatal accident occurred in one of the HC units that was part of the original Tokuyama Phase-2 part of the site. There is also no way to know if Tokuyama was aware of the KAM HC vessel failure; if Tokuyama made changes to the Company A HC vessel mechanical design; if Tokuyama was even aware of the details of grid attachment and, finally, if OCI made any changes in design of the grid attachment once they purchased the site.

There was another problem associated with the Company A HC FBR design supplied to KAM that may have contributed to the May 2010 failure. The individual grid hole design originally specified by Company A and which KAM used to fabricate the HC reactors resulted in very high pressure drop across the grid. KAM made several short attempts to run the first HC FBR in April 2010 with the original Company A grid hole design. KAM changed the grid hole design prior to the May 2010 failure. The new KAM grid hole design worked to reduce the pressure drop. Operating the reactor with the original high pressure drop Company A grid hole design may have contributed to the failure of the circumferential grid to vessel seal welds due to excessive upward force.

Analysis – Anhydrous HCl Co-feed Pipe Failure

Failure of the pipe used to add anhydrous HCl (A-HCl) co-feed to the hydrochlorination (HC) ($Si + 2H_2 + 3SiCl_4 = 4HSiCl_3$) fluid bed reactor (FBR) could easily result in the fatal accident experienced by OCIM in August 2024. As described in an earlier document section, A-HCl can be added to the main gas feed line (see Figure 18) which enters the HC FBR under the grid plate. An alternate A-HCl addition point is directly into the HC FBR reaction mass above the grid plate (see Figure 19). The OCIM configuration of A-HCl feed is not known.

Failure of either A-HCl feed pipe configuration could result in the fatal OCIM August 2024 accident. The immediate accident severity would be greater if the A-HCl feed pipe was directly into the HC FBR reaction mass as described in Figure 19.

Refer to the analysis of main gas feed pipe failure previously discussed as the same principles apply to failure of either A-HCl feed pipe configuration.

Analysis – Hydrochlorination Fluid Bed Reactor Vessel Main Weld Failure
Correct fabrication of hydrochlorination (HC) fluid bed reactor (FBR) vessels from the normal material of construction, Incoloy 800H (UNS N08810) can be challenging especially as HC reactors have become physically larger. There is a very limited number of competent Incoloy 800H fabrication shops located around the world.

The details of Incoloy 800H HC reactor fabrication in terms of design following accepted pressure vessel codes such as American Society of Mechanical Engineers (ASME) Section VIII (see: https://www.asme.org/codes-standards/find-codes-standards/bpvc-viii-1-bpvc-section-viii-rules-construction-pressure-vessels-division-1/2023/print-book)and the associated details of how "raw" Incoloy 800H plate and forgings are assembled into a large industrial reactor are beyond the scope of this report. The global knowledge base related to reliable fabrication of Incoloy 800H vessels has greatly improved over the past 20-25 years. A lot of this is due to work to improve safety of ethylene crackers, which are also constructed of Incoloy 800H. One area of improvement has been a better understanding of stress relaxation cracking (SRC) (See, for example: https://asmedigitalcollection.asme.org/PVP/proceedings-abstract/PVP2020/83860/V006T06A069/1089550).

A chronic problem with many older Incoloy 800H HC reactor vessels fabricated before there was an improved understanding on SRC was failure of the main vessel welds (longitudinal and / or circumferential) on reactors that had been in extended service. In a few cases, failures were experienced with a brand new HC reactor that had not been placed in operation. The failures are cracks in the main vessel welds.

The company with the most experience with these SRC HC reactor vessel failures is Union Carbide / Advanced Silicon Materials. Several industrial HC reactors operated by Union Carbide and / or Advanced Silicon materials were found to have cracks in some circumferential and / or longitudinal main vessel welds. All of these cracks were found in routine mechanical integrity inspections during planned maintenance outages. There are no known process safety incidents associated with weld cracks. This strong safety record speaks to the rigorous mechanical integrity inspections combined with a clear understanding, especially with the original Union Carbide HC units in Moses Lake, Washington, USA of the unique hazards associated with the HC process.

There is a good reason that Union Carbide / Advanced Silicon Materials have a lot of experience with SRC in Incoloy 800H reactors. These HC reactors were those built in the 1980's and mid 1990's before larger advances were made in Incoloy 800H fabrication. The current generation of larger Incoloy 800H reactors placed in operation by REC Silicon in 2009 and 2010 (Moses Lake) and TianHong REC China JV in 2018 have experienced no known SRC problems. These reactors were all built by Verolme (Rotterdam, Netherlands) who was identified in the early 2000's as the leading global Incoloy 800H fabricator through their work on large Incoloy 800H ethylene crackers.

Historical data for the other long-time operators of HC reactors – Denal, Osaka Titanium, Tokuyama (all in Japan) – are not available. There are also no data to even confirm that the long-time Japanese HC operators used Incoloy 800H for reactor vessel fabrication. Data for operation of newer HC reactors in China, Korea and Malaysia are also not available.

A main weld crack resulting for SRC in an operating HC reactor COULD result in a catastrophic failure as experienced by OCIM in August 2024. The same scenario previously described for a breach of the HC reactor vessel caused by localized erosion from an internal grid plate weld crack would likely apply. As with the HC reactor vessel breach from grid weld failure, routine local and remote monitoring of the operating reactors SHOULD identify a vessel breach caused by SRC early enough to shut-down and de-pressure the HC before the crack becomes large and catastrophic. This comment is made based on the two known experiences of HC vessel breach caused by localized erosion from grid attachment failures described previously.

Failure to identify could easily result in a serious incident. As with the localized erosion caused HC vessel breach from grid attachment failure, if the hole becomes large enough, the incident becomes very severe and the hole / crack size will grow due to escape of high velocity gas containing abrasive reaction mass / ground MGS powder.

Analysis – Hydrochlorination Fluid Bed Reactor Vessel Nozzle Failure
Correct fabrication of hydrochlorination (HC) fluid bed reactor (FBR) vessels also requires great attention to the detailed design and installation of the various nozzles required for process piping, instrumentation and manway connections. With regards to the OCIM August 2024 fatal accident, HC FBR vessel nozzle failure as the cause is likely less of a chance than the other failure modes discussed (and summarized in Table 1). Three potential failure modes exist with the nozzles used on HC reactors:

A. Weld cracking – nozzle to main vessel attachment

Weld failure where the nozzle is attached to the FBR vessel is a special case of the previously discussed weld failures of main vessel longitudinal and / or circumferential welds. The standard method of nozzle attachment to most pressure vessels is the straight pipe section of the nozzle being welded to the vessel through a hole placed in the vessel wall just slightly larger than the outside diameter of the nozzle. This weld attachment to Incoloy 800H vessels has been found to introduce excessive stress at the weld attachment. Some fabricators, such as Verolme (Netherlands), have developed a modified nozzle design that reduces the stress present where the nozzle is attached to the vessel wall. Details cannot be provided in this document due to NDA obligations.

Of the three nozzle failure modes presented in this sub-section, this represents the most likely failure mode of the OCIM August 2024 fatal accident BUT lower overall probability than other failures modes discussed (main gas feed pipe for example).

B. Internal nozzle corrosion

First-hand experience during detailed HC vessel inspections during maintenance outages shows that the internals of some nozzles located above the HC FBR grid plate can exhibit an accumulation of reaction mass solids. These solids will be saturated with chlorosilanes. If these accumulated solids are not completely removed each time the HC FBR is shut-down and opened to the atmosphere, moisture (water; H_2O), from the atmosphere will be absorbed by the accumulated solids. The chlorosilanes present in the solids will react with the water to form hydrochloric acid (aqueous HCl) of high localized concentration. The aqueous HCl will be only present in the accumulated solids. When the HC FBR is restarted, localized HCl-induced corrosion of the nozzle internals will be accelerated with increasing vessel temperature.

If this cycle of not removing accumulated solids is allowed to repeat over time, the localized corrosion could result in eventual failure of the nozzle through chloride stress corrosion cracking. Given the normal use of nozzles with very significant wall thickness, this specific corrosion scenario may take many years to present a problem. This identical corrosion failure mechanism has been observed in specific cross-exchanger designs used on the off-gas of some industrial HC units.

C. Internal nozzle erosion

The design of any nozzle attached to the HC FBR above the grid plate that is used to introduce routine flows of gas or solids into the operating HC FBR reaction mass or to remove solids from the HC FBR can present a significant failure mode. The failure mode is localized erosion of the internal surfaces of the nozzle caused by action (direct contact) of abrasive mass / metallurgical grade silicon combined with a failure to routine inspect the nozzles for localized internal wear.

The failure risk can almost be eliminated by use of a modified nozzle design. The nozzles connected to the HC FBR vessel are designed to be larger than required diameter for process flows. A sacrificial "insert" is placed inside the HC vessel nozzle. The insert is designed to take all abrasive wear and can be easily replaced during planned maintenance outages.

The highest risk HC FBR nozzle is one connected to the ground MGS powder feed system. There are two MGS feed configurations for HC reactors. Original technology of the OCIM HC unit involved in the August 2024 fatal accident fed the ground MGS vertically into the top of the reactor. There is no reason to believe that the MGS feed system was modified when OCI purchased the Malaysia site from Tokuyama but, there is no way to confirm this statement. For purposes of this report, design of the MGS feed nozzle for the OCIM HC reactor involved in the accident is assumed to be located at the top of the reactor.

The second MGS feed configuration is through an angled nozzle on the side of the reactor above the normal reaction mass level. This design represents the highest risk of nozzle failure in an industrial HC FBR. By nature of the angled design, erosive wear of feeding abrasive ground MGS into the HC FBR by high-pressure hydrogen is concentrated on the bottom "quadrant" of the nozzle. First-hand experience with similar nozzle designs (not in HC units) indicates that erosive failure can be "rapid". Use of a nozzle insert in an angled, side-entry ground MGS powder feed nozzle is an extremely important design feature. Even if an insert is not used and there is rigorous inspection of the angled MGS feed nozzle to identify when the wear is below a certain level (well before having a hole worn into the nozzle), replacement / repair of the nozzle is not a trivial undertaking. Reliable weld repairs on Incoloy 800H vessels that have been in chloride service, such as an HC reactor, can be difficult.

Failure to inspect all HC FBR nozzles and remove accumulate solids during each HC unit shut-down when the HC FBR has been opened to the atmosphere comes back to poor overall site implementation of standard operating procedures.

Comments and Questions
The OCIM accident raises a lot of questions. It would be very helpful to the overall global polysilicon industry if OCIM would release a detailed accident report. Such a report can save lives in the future.

While reviewing relevant information to prepare this document, one general design feature stands out especially when the HC process unit is compared with the methylchlorosilane (MCS; silicone precursor) and direct chlorination (DC) trichlorosilane (TCS; $HSiCl_3$) (Si +3 HCl) processes. All of these industrial fluid bed reactions (FBR) (HC, MCS, DC TCS) involve operation of a pressurized reactor. The HC process operates anywhere from 20 to 30+ barg. The MCS and DC TCS reactors typical run at 2 – 3 barg.

Any hazards analysis of these processes always identifies as one major risk, a catastrophic failure of a pipe connected to the FBR vessel itself and subsequent de-pressure / de-inventory of the FBR contents to the atmosphere. The contents of the FBR include high temperature flammable gases (chlorosilanes, methylchlorosilanes, hydrogen), water reactive gases (HCl, chlorosilanes, methylchlorosilanes) and pyrophoric solids (MGS-based reaction mass). The pipe that is always identified as the main risk for failure is the off-gas line from the FBR or the FBR + internal first stage cyclone. This pipe is identified as the main risk because it always contains entrained, abrasive “fines” from the reaction mass. Failure of this pipe from internal erosion results in the de-pressure / de-inventory scenario. This is what happened at OCIM on 14-August-2024.

The hazards analysis usually then asks can an isolation valve be placed on the exit nozzle of the FBR or FBR + internal first stage cyclone and the answer is normally: “good idea but the required full-port valve that will work when required has not been invented”.

In the world of MCS and DC TCS, the hazards analysis is always extended to the other direct pipe connections to the FBR vessel. Namely, these are feed gas, feed solid and various purge connections. In all cases, these FBR vessel connections include a remote operated full port isolation valve generally connected to the FBR vessel nozzle. These valves are incorporated into various safety systems and can also be individually closed from the control room. The purpose of these valves is to provide immediate isolation of the FBR from the connected pipe (say, the main gas feed line to the MCS FBR) should the connected pipe suffer a catastrophic failure.

A review of various piping and instrumentation diagrams (P&ID’s) on file from various HC process designs shows that the only connected pipe to the HC FBR that has a remote operated isolation valve near the FBR vessel is on the MGS feed system. None of these P&ID’s from several companies show such a valve on the main gas feed line (hydrogen [H_2] and silicon tetrachloride [STC; $SiCl_4$], maybe anhydrous hydrogen chloride [A-HCl]) entering the bottom of the HC FBR. These P&ID’s include those from the KAM (Korea) plant that used technology purchased from Company A, which was also used by Tokuyama Malaysia (source of original technology of the OCIM accident HC unit).

Appendix A

Bintulu, Sarawak, Malaysia
Site History:

Tokuyama
OCI Malaysia

Bintulu, Sarawak, Malaysia Polysilicon Site History

A. Tokuyama era

The current OCIM polysilicon site was originally developed by Japanese polysilicon producer Tokuyama. Tokuyama has operated a Japanese plant for many years and is one of the long-time qualified suppliers of semiconductor grade polysilicon to the global semiconductor industry. When the initial massive demand for solar-grade polysilicon began in the 2000's, Tokuyama decided to enter the solar polysilicon market with a greenfield plant located in Malaysia. The main reason that Tokuyama selected Malaysia (specifically Sarawak state) was access to low cost, low CO_2 hydroelectric power (compared to high cost, fossil fuel based electricity in Japan). Area development also included at least one MGS smelter that would take advantage of the same low-cost hydroelectric power.

The Tokuyama Japan polysilicon plant uses direct chlorination (DC; $Si + 3HCl$ ✍ $HSiCl_3 + H_2$) as the main route to production of trichlorosilane (TCS; $HSiCl_3$). By-product silicon tetrachloride (STC; $SiCl_4$) from the DC synthesis route ($Si + 4HCl$ ✍ $SiCl_4 + 2H_2$; $HSiCl_3 + HCl$ ✍ $SiCl_4 + H_2$) combined with by-product STC from the TCS-based Siemens polysilicon production route is primarily used by Tokuyama to produce fumed silica. Fumed silica is nano-sized SiO_2 produced by burning STC (other feed materials such as TCS and methyltrichlorosilane [CH_3SiCl_3; MTCS; M1] can also be used by Tokuyama predominately uses STC). Excess STC not required for fumed silica production is converted back to TCS via a low-pressure HC TCS synthesis process. The Tokuyama HC reactor runs at 10 barg (this is very low pressure; most industrial HC units run at 20 to 30 barg).

Tokuyama is a major regional supplier of fumed silica. Their main non-Chinese regional fumed silica competitor is OCI Korea. The main use of fumed silica is in production of a wide range of silicone products including sealants, rubbers and gums. Fumed silica is also used in many non-silicone products including adhesives, paints and pharmaceuticals.

Tokuyama is believed to have the majority of the global market for a special grade of fumed silica: "CMP grade". CMP = chemical mechanical planar and is a method used to polish single crystal semiconductor silicon wafers. CMP fumed silica is used as a polishing compound in the overall CMP process. CMP fumed silica purity must be very high; it is assumed that Tokuyama has a dedicated CMP fumed silica unit in Japan that uses high pure STC by-product from the TCS Siemens reactors.

Tokuyama did not use their own TCS synthesis technology for the Malaysia plant. This is likely because they recognized the need to produce TCS by hydrochlorination (HC) ($Si + 2H_2 + 3SiCl_4 = 4HSiCl_3$), instead of DC, to avoid having to handle by-product STC (the global fumed silica market can only handle a specific amount of fumed silica capacity). Tokuyama likely realized that their low pressure (10 barg) HC process was not suitable for high volume TCS production.

Tokuyama purchased at least HC TCS synthesis technology from a USA-based company that will be called Company A in this document. Company A may have sold technology for the remainder of the plant, except TCS Siemens reactors, but this is not clear. Tokuyama is believed to have used their own TCS Siemens reactor technology.

Tokuyama announced Phase-1 of the Malaysia site in August 2009 with a capacity of 6,200 TPY semiconductor grade polysilicon. Some analysts speculated that Tokuyama had planned to move all semiconductor grade polysilicon production from Japan (high energy cost) to Malaysia as there was no identified incremental increase in global semi industry demand to justify the 6,200 TPY capacity. Initial startup of Phase-1 was the 1Q 2013. Tokuyama announced Phase-2 of the Malaysia site in My 2011 with a capacity of 13,800 TPY solar grade polysilicon. Phase-2 started in October 2014.

Tokuyama shutdown the entire Malaysia site (Phase-1 and Phase-2) in November 2014. The reason given by Tokuyama was chronic quality problems associated with production of semiconductor grade polysilicon in Phase-1. Perhaps the main reason is that by the time Phase-2 solar grade poly production started, the first wave of significant Chinese solar grade polysilicon capacity was already happening with the result being depressed solar grade polysilicon prices and failure of many Chinese and non-Chinese solar grade polysilicon plants. Hemlock abandoned their 95+% complete 15,000 TPY solar grade polysilicon plant in Clarksville, Tennessee, USA in late 2014 due to Chinese over-capacity.

1) *Company A Technology provider for TCS-based Polysilicon: DETAILS*

   Company A was a small company with several employees. Some of the employees had previously worked at the Moses Lake, Washington, USA polysilicon plant during the Advanced Silicon Materials (ASiMI) ownership period and for Mitsubishi Polysilicon (now High Pure Silicon; Theodore, Alabama). The HC technology sold by Company A to Tokuyama represents a second "wave" of Company A technology sales.

   Company A initially sold their complete turn-key technology (including TCS Siemens reactors) to Chinese and Korean companies in the 2006-2008 time frame. One company was Korea Advanced Materials (KAM; 50-50 JV between KCC and Hyundai Solar). The author of this document worked on the KAM polysilicon plant from mid 2009 to 2012. Any technology sold to Tokuyama for the Malaysia plant is assumed to be very similar, if not identical, to the technology sold by Company A to KAM with the notable exception of individual HC TCS synthesis unit capacity.

   The original HC TCS synthesis technology of Company A was a close copy of the original Union Carbide HC TCS synthesis technology built and operated in Moses Lake, Washington, USA. The HC technology sold to KAM by Company had the same nameplate individual HC reactor capacity and included some features "unique" to the original Moses Lake HC units.
   The grid plate and design of individual grid holes used by Company A was loosely based on the very reliable Union Carbide grid hole design. The Union Carbide grid hole design does a very good job to minimize sifting of MGS powder from the area

above the grid to the rea below the grid. This design is still assumed to be used in all HC FBR's currently (late 2024) operated by REC Silicon. The Union Carbide grid hole design is proven to minimize the amount of solids sifting through the grid holes and into the area under the grid plate.

Company A's original grid hole design was similar to the proven Union Carbide design but deviated in two very important ways. These changes may have been made to avoid selling a direct copy of the Union Carbide design? Company A may have made these changes without fully understanding the original Union Carbide design and subsequent review by the original site owner Tokuyama and the current owner OCI did not recognize the problem.

One change was the design for entry of gas from under the grid, through the individual grid holes and into the reaction mass. The other change was the total number of grid holes. These deviations from the original Union Carbide grid hole design may have contributed to excessive pressure drop across the entire grid and may have contributed to higher than desired amount of solids sifting through the individual holes. Additional details and comparisons cannot be provided. These differences, if still present in the currently operated OCIM HC reactors, could have contributed to an excessive amount of MGS being present below the grid. A full engineering study would be required to pass final judgement.

Company A, at least with the overall design sold to KAM, did not include co-feed of anhydrous HCl (A-HCl) recovered from the Siemens reactor off-gas recovery (OGR) back to the HC TCS synthesis reactor. The design sold to KAM included two smaller capacity TCS DC (Si + HCl) units that were designed to consume the A-HCl. The KAM design included use of both HCl and STC as make-up Cl for the site. A-HCl co-feed to the HC units was not included as Company A reported they did not have the necessary expertise required. Company A made a wise decision, in the opinion of this document's author, by not designing their HC units to include A-HCl co-feed due to lack of published corrosion data for the systems H_2-STC-HCl and H_2-STC-HCl-Metallurgical grade silicon.

Company A also specified use of the same low fines content (where fines are particles less than 75 microns) ground MGS as used by Union Carbide / ASiMI / REC Silicon and almost all new HC unit operators.

The status of A-HCl co-feed with the Tokuyama Malaysia polysilicon plant is not clear. By the time Company A sold HC technology to Tokuyama, there were examples of Chinese polysilicon producers operating Chinese-designed HC units with A-HCl co-feed. Google Earth analysis of the Malaysia site shows a possible trichlorosilane (TCS; $HSiCl_3$) DC ($Si + 3HCl \rightarrow HSiCl_3 + H_2$) unit adjacent to the two HC units of Phase-1. This TCS DC unit could have been designed to handle all A-HCl from the Phase-1 and Phase-2 Malaysia plants.

The HC unit design sold by Company A to KAM had an equivalent polysilicon capacity of 1,500 metric tonnes per year (TPY). KAM polysilicon capacity was 3,000 TPY so there were two HC units. This is close to the nameplate capacity of the original Union Carbide Moses Lake site.

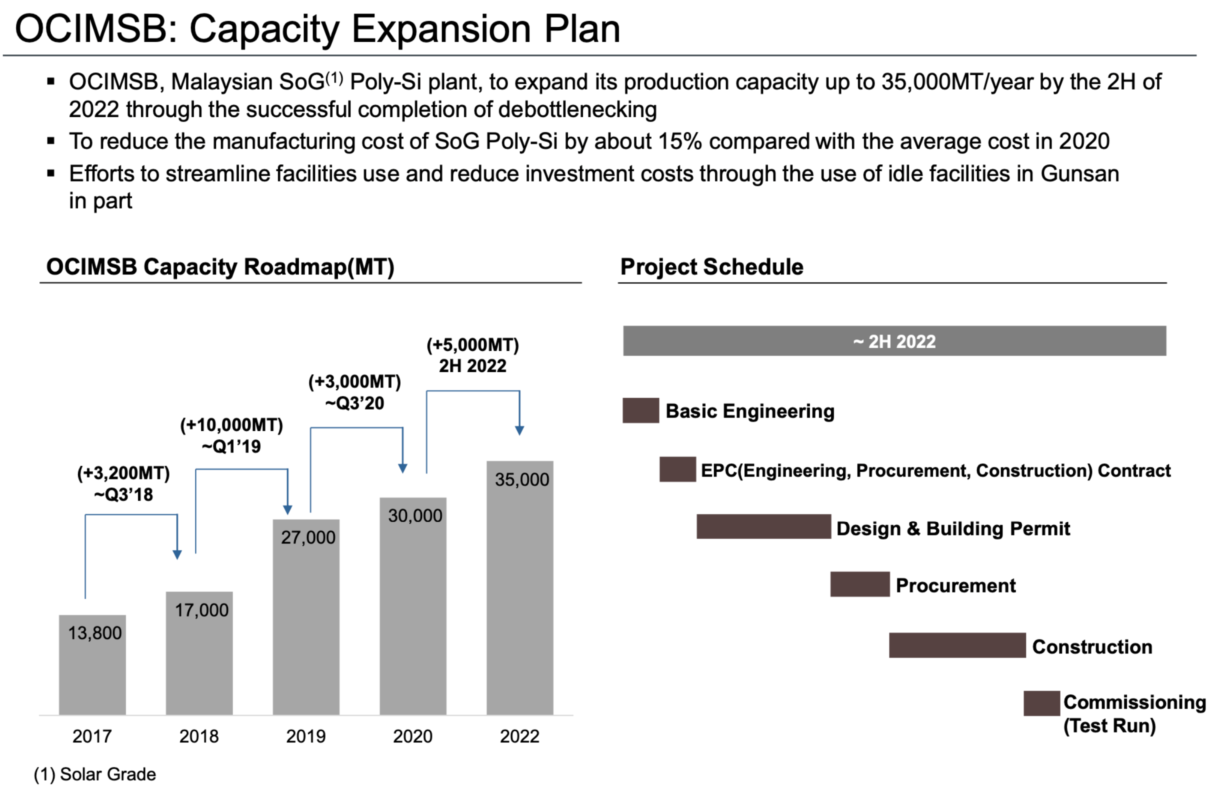
Tokuyama Malaysia Phase-1 capacity was 6,200 TPY and Google Earth clearly shows two HC units. The HC units are distinctive as they include a covered structure above each HC FBR. The covered structure contains the ground MGS feed system (hoppers and filter). Individual HC unit capacity = 3,100 TPY equivalent polysilicon. Phase-2 capacity was 13,800 TPY and Google Earth clearly shows four HC units. Individual HC unit capacity = 3,450 TPY equivalent polysilicon. The HC units sold to Tokuyama probably had a nameplate capacity of 3,500 – 4,000 TPY polysilicon.

B. <u>OCI Era</u>

OCI announced on 28-September-2016 that they would purchase the Malaysia site from Tokuyama for cents on the dollar. The Malaysia site failure had come close to bankrupting all of Tokuyama. OCI total solar grade polysilicon capacity was 52,000 TPY at their Gunsan, South Korea site at the end of 2015. OCI was feeling the pressure of Chinese over-capacity combined with high Korean electricity prices. OCI's purchase of the Malaysia site was a very good long-term strategic decision. OCI Korea stopped production of all solar-grade polysilicon in February 2020 and re-focused Gunsan operations to produce 6,500 TPY nameplate capacity semiconductor grade polysilicon. Solar grade polysilicon production was shifted to low-cost (hydroelectricity) Malaysia.

OCI announced closure of the deal with Tokuyama on 26-April-2017. OCI restarted Phase-2 and was operating at the Phase-2 nameplate capacity of 13,800 TPY solar grade polysilicon by the end of 2017. OCI began an aggressive program to add capacity to the Malaysia site through de-bottlenecking of the original Tokuyama units and addition of new HC capacity, presumably based on OCI Korea technology. The following summary of these programs was taken from a OCI Holdings report (download found here: https://www.oci-holdings.co.kr/en/ir/library?currentPage=4).

Figure 25: OCIM capacity expansion plan published 23-December-2020 by OCI Holdings.



The + 10,000 TPY Q1 2019 expansion is assumed to be construction of one or two new HC unit(s). The latest Google Earth image 5-May-2020 shows the likely new HC unit(s) adjacent to the original four Phase-2 HC units. The remaining expansions are assumed to be debottlenecking of all HC units combined with additional TCS purification, Siemens reactor, off-gas recovery and product finishing capacity.

Unknown are the details of the debottlenecking changes made by OCI to the original six HC units supplied by Company A to Tokuyama. OCI Korea HC technology is from an obscure technology provider that has no additional presence in the global polysilicon industry. Details of the OCIK technology, such as grid plate hole design, are not known.

Given the 14-August-2024 OCIM accident and the November 2024 information suggesting the root cause as erosion of accumulated MGS in the main gas feed line, did OCI change the original Union Carbide style grid hole design to the unknown OCIK grid hole design as part of the debottlenecking projects? Does the OCIK grid hole design enable more solids to sift through the grid?

Figure 26 shows the most recent Google Earth image of the entire OCIM site (5-May-2020) Figure 27 shows details of major process units in Phase-1 and Figure 28 shows details of major process units in Phase-2 including the new HC unit(s) built by OCI in 2019-2020. The GPS coordinates are 3°32'35.29" N 113°18'34.28" E.

Figure 26: Overall OCIM site. This is the most recent (as of November 2024) Google Earth image of the site dated 5-May-2020.

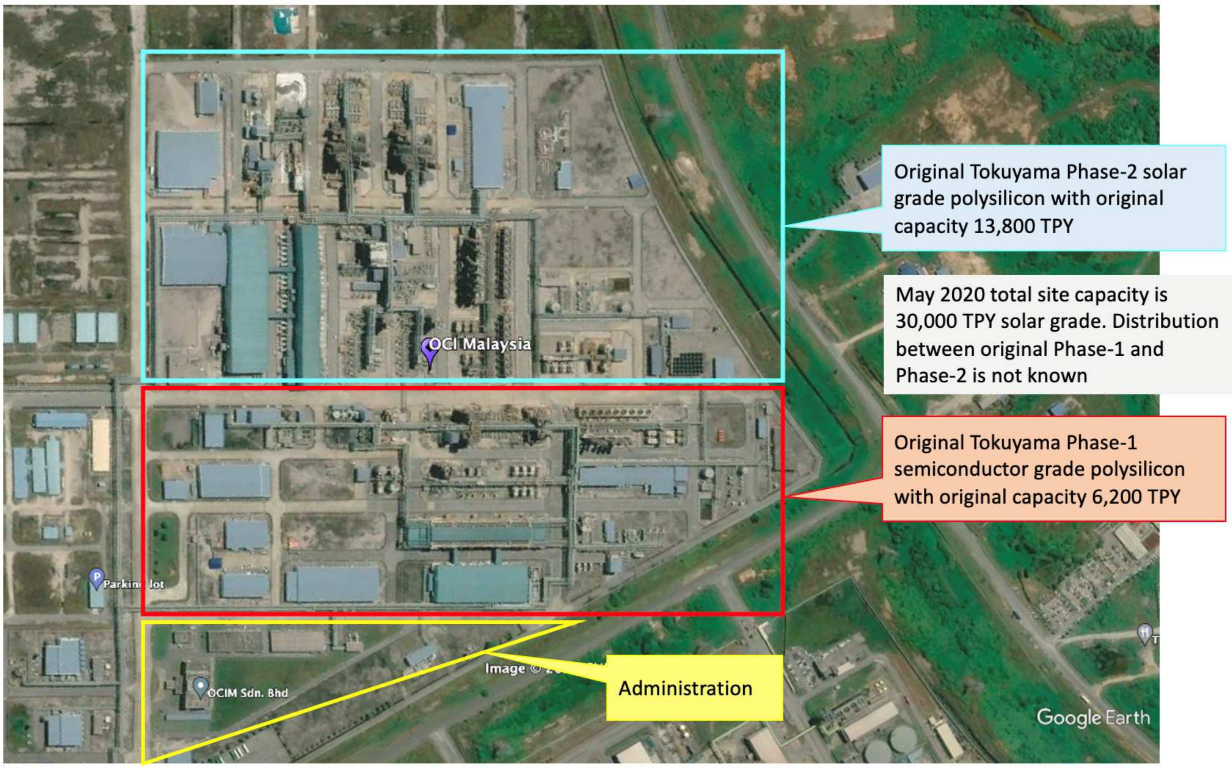


Figure 27: OCIM Phase-1 site with major process units identified. This is the most recent (as of November 2024) Google Earth image of the site dated 5-May-2020.

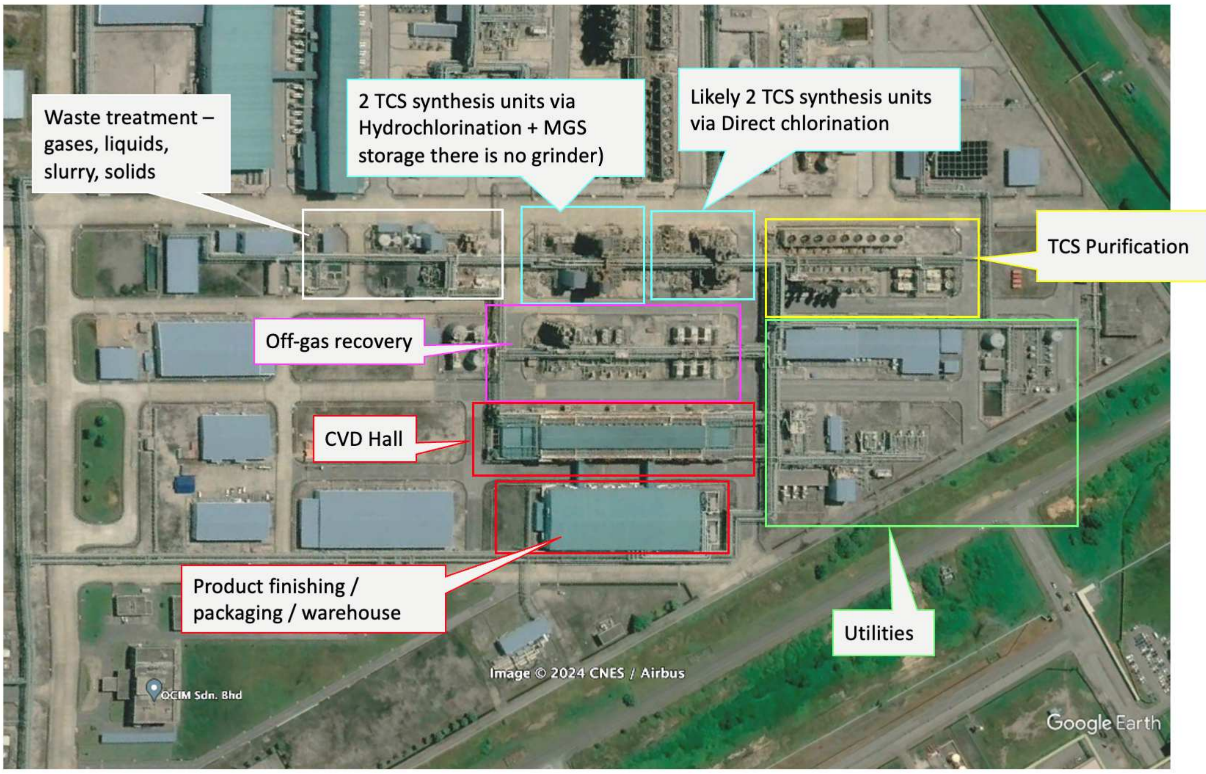


Figure 28: OCIM Phase-2 site with major process units identified. This is the most recent (as of November 2024) Google Earth image of the site dated 5-May-2020.