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Considerations for polysilicon plant expansions and upgrades

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ABSTRACT

As polysilicon producers perform expansions and upgrades to increase production and improve operations, plant safety remains critical. Companies should routinely review their safety policies and effectively plan their projects to ensure uninterrupted product supply and create a safe environment for employees and the communities in which they operate. Both the design and the execution of expansion and upgrades to projects are critical as companies strive for minimal down time so that productivity is not affected. Such hazards and scenarios that may hinder and delay start-up, specifically in relation to polysilicon plants, are highlighted in this paper. Furthermore, the paper outlines how best to avoid these situations, offering methods of execution to achieve the three key measures of success: safety, high purity and minimal downtime.

Review of chemical hazards

This section reviews the hazards of the chemicals that are used in a polysilicon plant every day, and as a result may be assumed as safe. Polysilicon production requires the use of several hazardous chemicals, including trichlorosilane (TCS), dichlorosilane (DCS), and hydrogen (H_2), which are highly flammable. Silicon tetrachloride (STC) is corrosive when exposed to moisture. Some plants use hydroflouric acid (HF) and nitric acid (NHO_3) for polysilicon etching or pipe cleaning. In some processes, pyrophoric (self-igniting in atmospheric moisture) polymers and precipitates are generated, creating another hazard.

This summary reinforces the need for careful review of the applicable Material Safety Data Sheets (MSDSs) especially during expansion and maintenance projects, which bring huge potential for releases, fire and exposure. In regard to the chemicals discussed in the following sub-sections, general fire fighting recommendations are to use positive pressure self-contained breathing apparatus and full fire-fighting turnout gear.

STC

STC is a non-flammable liquid that reacts vigorously with water to form hydrogen chloride (HCl). The reaction of STC with water can form dense white clouds of silica particles and hydrogen chloride fumes. Hydrogen chloride may then in turn react with metal, producing highly flammable hydrogen. Hydrogen chloride vapours are extremely irritating and burn skin and eyes on contact. In the case of a release, personnel should evacuate from the danger area.

TCS and DCS

TCS and DCS are flammable liquids or vapours depending on storage conditions. The boiling point of TCS is 31.9°C, while DCS is only 8.4°C. TCS and DCS ignite with a rapid flashover at the liquid surface and generate very little or no noticeable flames. Burning DCS and TCS produces HCl and possibly H_2 in the white smoke of SiO_2, but only small amounts of radiation heat.

"Proper design and precautions for fire prevention are extremely important."

The best way to extinguish a TCS or DCS fire is to stop its flow, as attempting to extinguish the fire without stopping the flow may permit the formation of explosive mixtures with air. Foam (water with 6% solution of Hazamat II foam) is the recommended extinguishing medium. The use of foam reduces spreading of the flammable liquid and reduces the temperature of reaction, mitigating the incident. The water in the foam will react to create the by-products hydrogen and HCl, possibly creating hydrogen bubbles in the foam which can ignite during clean-up. There is always a high risk of re-ignition after extinguishing these fires. The HCl created in the foam is corrosive and its discharge may be restricted. A facility that houses such processes is best designed for containment with the grade sloped toward collection points.

Proper design and precautions for fire prevention are extremely important. This not only includes the design of equipment to prevent release, but also the implementation of measures to minimize sources of ignition. These include:

- Personnel ban on smoking
- Ventilation to remove vapours
- Design sloped surfaces to collection points away from equipment and buildings
- Use of electrical classifications for certain equipment
- Purge and inert equipment and containers
- Control static electricity
- Control cutting, welding and other "hot work"
- Control other potential ignition sources.

Silane (SiH_4)

Silane (SiH_4) is pyrophoric and spontaneously reacts with oxygen in air at concentrations greater than 3 mol % (molar percent), resulting in fire. Silane, a dual hazard to health and flammability, can be handled safely as long as proper design, construction and maintenance are implemented. In addition to the recommendations for DCS and TCS, the following actions should be considered:

- Bond and ground all lines and equipment

Figure 1. Crushed polycrystalline silicon.

Figure 2. Engineer working in a plant wearing appropriate safety gear.

- Use restrictive flow orifices (RFOs) to control the purge for anything containing silane
- Install thermal sensing devices and alarms
- Require personnel to use self-contained breathing apparatus.

Hydrogen and hydrogen chloride

During maintenance activities when flushing and purging vessels or piping, it is important to remember that TCS and DCS react with water to produce hydrogen and hydrogen chloride. Care must be taken even when dealing with leaks of TCS and DCS due to the presence of hydrogen. During leaks, moisture in the air can produce hydrogen and hydrogen chloride.

Both anhydrous hydrogen chloride and hydrochloric acid are extremely corrosive. Hydrogen chloride is corrosive and irritating to the eyes, skin and mucous membranes. Inhalation may result in lung damage and water in the lungs and could be fatal. HCl can also attack most materials of construction in the presence of moisture, and reacts with many metals to release hydrogen gas. Careful planning should be made such that HCl contact with incompatible materials is avoided. It is best to control HCl maintenance activities so that any releases are directed to a scrubber.

Hydrogen is extremely flammable: with a lower explosive limit (LEL) of 4 vol % and an upper explosive limit (UEL) of 74.5 vol%, hydrogen can easily cause an explosion. As it burns with an invisible flame and gives off low thermal radiation, fires involving hydrogen may not be immediately detected and personnel may unknowingly enter a fire area. If a hydrogen fire occurs, the source of the leak must be isolated since fire-fighting methods may not stop an immediate recurrence.

Cleaning and passivation fluids

Piping and equipment are chemically cleaned and passivated to prevent process contamination. The chemicals used are aggressive in leaching impurities out of base metals in a controlled environment. These chemicals are highly corrosive and/or toxic.

Caustic (~50% sodium hydroxide)

Caustic is typically used to remove scale and organics from new, unused carbon steel. Due to exothermic reaction and splash risks, caustic must always be added to water slowly and in small amounts – never add water to caustic. Additionally, care should be taken to ensure only proper materials contact the caustic solution. Aluminium, zinc, or materials galvanized with zinc can produce hydrogen gas.

Caustic will cause severe burns and deep ulcerations on direct contact with skin. Eye contact may cause blindness. Inhalation can cause severe respiratory damage. Therefore, the work area where caustic solutions are being used should be well ventilated. Workers and spill responders should wear impervious gloves, boots, coveralls, goggles, full-face shield, and a NIOSH/MSHA-approved self-contained respirator when in close proximity to the container.

Dilute hydrochloric acid

Hydrochloric acid is typically used to etch carbon steel to remove free iron from new carbon steel already treated with a caustic solution or re-used carbon steel after proper decontamination. The safety issues mentioned herein regarding hydrochloric acid should be adhered to in these cases.

Dilute hydrofluoric acid

Hydrofluoric acid (HF) is used to etch stainless steel and is highly toxic. In low concentrations, exposure to HF may not be noticed for up to 36 hours. However, upon initial contact, health treatment must be initiated immediately or the exposure can be fatal, as HF penetrates human cells and rapidly dissociates into hydrogen and fluoride ions. The fluoride can penetrate and bind with calcium, magnesium, sodium, and potassium in the human body. The result is demineralization and systemic deficiency of calcium and magnesium with excess potassium. Because of the potentially life-threatening defects resulting from such exposure, medical treatment should be sought immediately.

Due to the severity of the hazards involved with hydrofluoric acid and the inability on the part of the affected subject to feel immediate contact, it is recommended that a dilute solution of HF with dilute nitric acid (HNO_3) be used. The HNO_3 provides an immediate burning sensation indicating when exposure has occurred, prompting immediate attention.

Workers and response personnel should be well trained in proper first-aid use and proper application of calcium gluconate gel for HF exposure as, for example, excessive application of calcium gluconate to the eyes can cause permanent blindness.

Dilute nitric acid

Nitric acid (HNO_3) is a strong oxidizer used for passivating stainless steel. HNO_3 is also extremely corrosive in the presence of aluminium and copper, and reacts violently with water to generate heat and toxic, corrosive, and flammable vapours. A water mist will help to control the vapours, and residue can be neutralized with a dilute solution of sodium carbonate.

HNO_3 burns on contact and is easily absorbed through the skin and respiratory tract. Exposure, even below 2ppm, can cause skin burns and penetrating ulcers, sight loss if contacted with the eyes, gastrointestinal tract burns and perforation of the digestive tract if ingested, and respiratory tract burning and pulmonary oedema if inhaled. Among other dangers, repeated inhalation can cause chronic bronchitis and kidney failure. Even in low concentrations, exposure can be fatal.

Therefore, extreme care must be taken when handling HNO_3. Even in well-ventilated areas, workers should wear impervious gloves, boots, suit, goggles, full-face shield, and NIOSH/MSHA-approved self-contained respirators when in close proximity to the container. Responders should wear the same in addition to a self-contained breathing apparatus.

Water

As discussed, water reacts with chlorosilanes to produce hydrogen and hydrogen chloride. However, another reaction product that must be taken into consideration is silicon dioxide. When starting up systems after a maintenance activity, equipment should be dried to a low dew point in order to avoid the corrosiveness of HCl and the damage it causes to the structural integrity and high purity condition of the equipment. This action also limits the formation of silicon dioxide which can form precipitates that clog up equipment, reduce the available surface area of heat exchangers, or spin around in pumps like shot blast until the pump casing is damaged. Therefore, it is very important to verify that all equipment and piping is drained and dried before going back into service.

We don't know what the stuff was, but it's pyrophoric!

Although the MSDS might not have documented advice and safety on each and every compound, there have been enough safety-related incidents in this industry to support the assumption that any piece of equipment in the TCS production and first stages of TCS purification may contain pyrophoric precipitates. Some reboilers are known to have them, and the design may include double block and bleed valves and spares for ease of maintenance, while others have no design features to accommodate the situation.

> "Any piece of equipment in the TCS production and first stages of TCS purification may contain pyrophoric precipitates."

The standard procedure prior to a maintenance activity is to drain the equipment, and purge it out with nitrogen prior to opening. It is possible to bleed a little steam into the nitrogen to see if there is a temperature rise in excess of the steam addition, indicating the presence of a pyrophoric compound. If a temperature rise does occur, one option is to continue the steam bleed until the compound burns itself out, but often that may take too long. Some prefer to close up the equipment, move it to a special fire watch yard equipped with a scrubber, and let it burn itself out in a controlled situation. Additional strategies are discussed in the following sections, but whatever the approach and whatever the strategy, a flaming condenser should not be taken off the top of a tower at any time.

Review of safety regulations and standards

There are many regulations provided by various governmental authorities and industry associations that cover the safe practices of designing and dealing with the hazardous chemicals of our industry. A partial list of standards providers includes those listed in Table 1.

Hazard Communication – U.S. Department of Labor, Occupational Safety and Health Administration (www.osha.gov)
NIOSH Pocket Guide (www.cdc.gov/niosh)
High Pressure Gas Safety Law of Japan KHK, Sumitomo-Tranomon Bldg., 4-3-9 Toranomon, Minatoku, Tokyo 105-8447
Toxic Gas Ordinance No. NS-517.445, Santa Clara County, California
The EEC Safety Sheets Directive 93/112 EEC
NFPA Standards, National Fire Protection Association, 1 Batterymarch Park, PO Box 9101, Quincy, MA 02269
SEMI Standards (Semiconductor Equipment and Materials International), 3081 Zanker Road, San Jose, CA 95134
SEMATECH (SEMATECH Inc./International SEMATECH Inc.), 2706 Montopolis Drive, Austin, TX 78741 (www.sematech.org)
Compressed Gas Association, 1725 Jefferson Davis Highway, Suite 1004, Arlington, Virginia 22202
Uniform Fire Code, UFC, 5360 South Workman Mill Road, Whitter, CA 90601
The High Pressure Gas Safety Institute of Japan (KHK), Application Guide for the High Pressure Gas Safety Law
SSA Journal, Volume 11 No. 4, Winter 1997, SSA Journal Headquarters 1313 Dolly Madison Blvd. Suite 402, McLean, VA 22101
Factory Mutual Property Loss Prevention Data Sheets, Factory Mutual Engineering, PO Box 9102, Norwood, MA, 02062 (www.fmglobal.com)
Centre Européen des Silicones (CES), Avenue E. van Nieuwenhuyse 4, Box 2, B-1160 Brussels – Safe Handling of Chlorosilanes Material Safety Data Sheets

Table 1. Partial list of providers of standards for designing and dealing with hazardous chemicals in the PV industry.

Methods of planning for safe expansion

Proper expansion planning begins at the design stage of the original plant. Engineers must anticipate the need for future expansions and improvements as bottlenecks and design limitations are identified in the design phase of the original plant design, or subsequent expansion designs. Statements such as, "We will buy TCS and install a TCS Synthesis Unit later", or "Throughput of the Purification Unit is limited to 120% of design capacity, but our next phase will be 200% of current capacity", are common during original design phases. Others ask, "Do we modify the existing Off-Gas Recovery to increase capacity or duplicate the existing design?" or similar questions. These considerations underscore the need to plan the expansion in the original plant design.

Regardless of the considerations, one point is vital: do not restrict the options. Good plant designs provide flexibility to anticipate expansions and modifications without restricting options or disrupting ongoing operations.

The cost of planning for an expansion that might not occur for years can be difficult to take on board. Value engineering may try to limit the number of valves to reduce cost. A DN200 split-

Figure 3. It is critical that the controller coordinate the plant expansion work with the personnel for the areas impacted.

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Figure 4. Chemical plant fire.

body stainless steel ball valve can be very expensive in itself. Cleaned for high purity service in a double-block-and-bleed arrangement, two DN200 valves and a DN25 drain valve are extremely expensive. However, compared to stopping production, decontaminating, purging, installing the modification, cleaning, purging, and re-starting in order to make a tie-in for an expansion, the payback is immediate the day the pre-installed expansion valves are finally used. Since the existing system is not opened to atmosphere or exposed to construction activities, the risk of injury from corrosive or flammable contents is reduced, and operating product purity is not sacrificed.

> "Good plant designs provide flexibility to anticipate expansions and modifications without restricting options or disrupting ongoing operations."

This only works if the designers have the forethought to install tie-in valves in the required location, assuming the valves, piping, and equipment were sized for the increased capacity. For example, Dynamic Engineering was requested to reduce a header size from DN200 to DN150. Considering the owner's long-term production objectives, the options were presented as follows: 1) installing another DN150 pipe in a congested pipe rack later on in the expansion, or 2) keep the planned DN200 pipe with tie-in valves. The owners lamented the additional cost, but decided for flexibility. Two years later, the owners were praising their forethought.

Another consideration is installing flange connections at direction changes in the piping, which provides an easy location to tie in without cutting and welding. The downtime required to install a prefabricated, pre-cleaned, flanged spool versus a welded assembly is significant. Considering the impact on product quality, cutting and welding on pure process systems always diminishes product quality.

Not everyone's crystal ball can forecast the future needs of a plant. Tie-ins to existing operating systems are inevitable. With proper planning, design, decontamination, logistics, coordination, and control, the tie-in can be accomplished safely and quickly while minimizing effects on plant quality.

During a tie-in, the first thought should be to avoid hazardous chemical exposure. Care must be taken to decontaminate the system and create an inert atmosphere. Depending on the specific hazard, the process chemical(s) must be removed. Systems that are suspected to contain pyrophoric polymers should be flushed with STC, the remainder of which can then be heated and vented to the scrubber. STC works well to pacify and to soften the various pyrophoric polymers. The system can then be purged with nitrogen until acceptable testing conditions are met. Similarly, other hazardous systems can be drained and purged with dry nitrogen until acceptable testing conditions are met.

After decontamination, care should still be exercised. Always assume that the full hazard is still present. Refer to the MSDS for proper personnel protective equipment. Fireproof blankets, fire extinguishers, flange covers, and emergency medical personnel should be at the work site during tie-in activities. The system should be broken at flanges to ensure that residual liquids are removed, and the flange facings should then be immediately covered with fireproof blankets. Bear in mind that the system is an oxygen-deficient environment.

Construction begins

Once the expansion needs and hazards have been identified, construction activities are ready to begin. All materials – be they definitely required or not – should be staged to accomplish the goals for all projects in the area with minimum relocation effort. Only trained, experienced, supervised personnel should be employed when working these hazardous or pure process systems. An experienced controller should coordinate to accomplish the project goals as safely and quickly as possible. To ensure the multi-faceted project is orchestrated, the controller should communicate the plan and review with all plant personnel and contractors involved. Everyone needs to understand their role, and how it affects others.

Planning begins months before the event. The coordinator needs to request that all plant and project managers submit their requests three months in advance, or earlier if long lead items are required. Ten weeks ahead of time, the initial list of activities should be distributed. Production and project managers, supervisors, operators and maintenance should be involved in the review process, and 'finalize' the plan four weeks ahead of time. Instrument and equipment failures will occur after the plan is 'final,' and will need to be addressed. These should be anticipated by allocating space and resources to accommodate the unknown.

> "Once the expansion needs and hazards have been identified, construction activities are ready to begin."

The second step of planning after the activities are defined is the dedication of specific areas for them such as equipment lay down, hot work zones, acid washing, staging for bulk nitrogen trucks, routing for temporary scrubber connections, and any other requirements. These should be assigned to specific areas to allow emergency access to all of the plant. Timing of these activities also needs to be considered to prevent activities from interfering with each other.

Finally, a logistics safety and contingency plan should be developed, taking into consideration each activity and potential hazards. For example, a condenser may have unknown pyrophoric precipitates that catch fire when opened. In such a case, fire equipment should have been staged, and the lay down area situated so the smoke plume does not prevent workers from accessing their work.

During expansions and upgrade projects, the perceived success or failure of a project might have nothing to do with the design or construction of the project. The success of a project is often determined by the time required to meet purity requirements, but the rewards of a fast-track project are wasted if the short cuts taken cause extensive delays (sometimes up to several months) for the system to reach acceptable purity. Furthermore, expansions and upgrades that interact with existing production may jeopardize its previously reliable quality. If a project is completed ahead of schedule and under budget, but the resulting polysilicon quality is not suitable for sales for several months, the project would be deemed a failure.

In order to ensure project success, after pressure testing, a thorough cleaning procedure should be used to minimize time to product purity and maximize reliability of results. There are several qualified procedures available for cleaning metals for high-purity applications. For example, ASTM A967-05e has procedures for cleaning stainless steel in high-purity applications. However, in selecting a specific procedure, care must be taken to ensure that the chemicals and components used do not introduce undesired contaminants. Some ASTM A967-05e procedures allow the use of stabilizers and inhibitors which may contain phosphorous, an impurity of concern for polysilicon. Each chemical and application should be evaluated for the required results.

Cleaning equipment and piping for high-purity service will be wasted if not properly protected. The chemicals used for cleaning and passivation must be thoroughly removed. Simply flushing with water may not remove the residual from the grain structure of the metal. Steam cleaning is often used to flush any embedded, residual chemicals from within the metal grain structure, a step that should be followed immediately by drying with inert gas. Omitting this step might cause localized embrittlement and premature failure. Finally, the dried system should be sealed under a positive pressure, inert environment to prevent moisture ingress or airborne contamination. Whether using a dip-cleaning or circulation method, these steps are required to ensure long-term operation of the process with minimal time to reach product purity.

A start-up, whether for a new plant, expansion or upgrade, is challenging enough for any chemical process. Commissioning activities, the urgent need to start production and lack of experience in operating a new system add to safety concerns. The plant must be assembled cleanly, commissioned without leaks, started up without incidents and must produce a high-purity product in a timely manner.

Similar to the design and construction phases of a project or expansion, nothing is better for start-up than early and thorough planning. Successful planning should include the following: a detailed start-up program; sufficient people and resources on hand prior to start-up; training that covers the new process; a contingency plan for upsets and emergencies; a commitment from management to allow time to effectively complete the project.

After cleaning and inert verification, start-up of a polysilicon process employs the steps of introduction of chemicals, circulation and production. Each must be thoroughly planned and communicated to every member of the start-up team. Any shortcut or omission can create problems that would require maintenance, and consequently the re-introduction of potential for exposure and contamination.

Upsets and emergencies create the greatest potential safety concerns during a start-up. Operator training must include not only the specialized procedures for high purity operation, but response to upsets and emergencies to prevent chlorosilanes release or equipment damage. Training programs should include standard operating practices that have been well reviewed with 'what-if' approaches of HAZOP.

Emphasis should be placed on handling the corrosive and flammable chemicals and the methods for achieving and maintaining high purity without sacrificing safety or efficiency. With so many new polysilicon manufacturing facilities under development, the experience necessary to handle upsets and emergencies may not reside with the employees in the plant. Use of experienced third parties can greatly reduce the learning curve both in the planning and operating stages.

Conclusion

Though polysilicon production brings with it a multitude of hazards, projects can be implemented to ensure product supply and create a safe environment for employees and the communities in which they operate. Execution planning is critical for projects to achieve the three key measures of success: safety, high purity and minimal down time.

In addition to the guidance provided herein, a producer should always consult with their local fire department, insurance carrier and any other regulatory agencies or body to ensure that they are in full compliance for local regulatory requirements for personnel and environmental protection. A steep learning curve is dangerous and costly.

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