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MANUFACTURE OF THIN-FILM PHOTOVOLTAIC CELLS: CHARACTERIZATION AND MANAGEMENT OF PHOSPHINE HAZARDS

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ABSTRACT

Phosphine is a highly toxic and flammable gas used in thin-film photovoltaic cell manufacturing. Its use can present serious occupational and public health hazards if appropriate prevention and control options are not effectively implemented. This report reviews technologies for controlling PH_3 emissions during routine operation and accidents, hazard prevention options, and emergency preparedness and response strategies. Routine PH_3 emissions can be controlled by using carbon adsorption for very low concentrations and chemical scrubbing for higher ones, but massive accidental releases are very difficult to control and could jeopardize the life and health of populations living near a plant. Options for preventing or minimizing accidental releases (e.g., flow-restricting valves) need to be implemented to reduce risks. Industry and community emergency response planning can further reduce the magnitude of these hazards.

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1 INTRODUCTION

This report characterizes potential occupational and public health hazards associated with the use of phosphine (PH_3) gas in manufacturing photovoltaic (PV) cells and reviews options for controlling these hazards. The potential use of PH_3 in significant quantities as a feedstock gas in future production of zinc phosphide (Zn_2P_3) thin-film PV cells may present large hazards both to occupational and to public health. The gas is used in small quantities as a dopant in existing PV cell industries (e.g., amorphous-Si), and here its high toxicity may present occupational hazards.

This study supplements previous hazard identification studies by the Biomedical and Environmental Assessment Division of Brookhaven National Laboratory [1-3]. It includes identification of the physical and chemical properties of PH_3 in pure form and in mixtures with other gases present in the industry; estimation of PH_3 quantities in storage and process systems; safety analysis of process and storage systems; assessment of worker interface with these systems; identification of public populations at risk to accidental and routine releases; and evaluation of occupational and environmental control needs, availability, effectiveness, and cost.

2 POTENTIAL HAZARDS

2.1 Health

Phosphine gas is an acute systemic poison and a severe pulmonary irritant. In occupational settings it has caused both sudden and delayed death due to pulmonary edema. Workers exposed intermittently to concentrations up to 35 ppm but averaging below 10 ppm may experience nausea, vomiting, tightness of chest, cough, headache, and dizziness. Single severe exposures may cause similar symptoms as well as excessive thirst, muscle pain, chills, and dyspnea. There is, however, no evidence of cumulative effects after exposure ceases [4].

Fifty-nine cases of PH_3 poisoning including 26 deaths were recorded between 1900 and 1958 [4]. More recent cases of PH_3 and arsine (AsH_3) poisoning in the metallurgical industry have been recorded [5]. Possible PH_3 exposures have been reported in the semiconductor industry [6] and in a PV cell manufacturing facility [7].

2.2 Safety

Phosphine may auto-ignite in air, even at 40 to 50°C, according to the following reactions:

$$2PH_3 + 3O_2 \rightarrow P_2O_3 + 3H_2O \ ,$$

$$2PH_3 + 4O_2 \rightarrow P_2O_5 + 3H_2O \ .$$

The combustion products, phosphorous trioxide (P_2O_3) and pentoxide (P_2O_5), are also highly toxic, but as solids they are easier to control. If PH_3 is mixed with hydrogen, the gas mixture may present an explosion hazard when it comes in contact with air, but the explosive limits of PH_3 or PH_3-H_2 mixtures are not known.

No information on PH_3 fire incidents was found in the literature. In such fires the occupational and public health risk due to the release of toxic gases and toxic by-products is probably greater than that due to the fire or explosion. In this report, emphasis is on hazards related to the toxicity of PH_3 and its by-products.

3 STANDARDS AND REGULATIONS

3.1 Occupational

The Occupational Safety and Health Administration (OSHA) has the regulatory responsibility for protecting workers from workplace hazards.

OSHA has established safe exposure concentration limits for several pollutants and has recommended handling practices for selected toxic substances. Additional voluntary standards for toxic materials have been developed by the American Conference of Governmental Industrial Hygienists (ACGIH) and the American National Standards Institute (ANSI).

OSHA has issued limits for average and short-term exposures to PH_3 as well as generic guidelines for respirator selection. Standards include a "Permissible Exposure Limit" (PEL) concentration of 0.3 ppm and an "Immediately Dangerous to Life or Health" (IDLH) concentration of 200 ppm. The PEL is the work-shift (8-hr workday or 40-hr work-week) time-weighted average (TWA) concentration to which most workers may be repeatedly exposed without adverse effects. The IDLH concentration, defined for the purpose of respirator selection, is the maximum level from which an individual could escape within 30 minutes without any escape-impairing symptoms or any irreversible health effects. The American Institute of Governmental Industrial Hygienists (ACGIH) suggests a time-weighted average "Threshold Limit Value" (TLV-TWA) of 0.3 ppm and a "Short-Term Exposure Limit" (STEL) of 1 ppm. The STEL is the maximum concentration to which workers may be exposed for a period up to 15 minutes, provided that no more than four excursions per day are permitted with at least 60 minutes between them and also that the daily threshold limit value is not exceeded [4].

3.2 Public

The Clean Air Acts of 1970 and 1977 assigned to the U.S. Environmental Protection Agency (EPA) the regulatory responsibility for controlling the discharge of industrial pollutants into the atmosphere: EPA is required to establish National Emission Standards for Hazardous Air Pollutants (NESHAPs) and to develop New Source Performance Standards (NSPS) for industries emitting large quantities of pollutants. EPA has not yet initiated development of national standards for atmospheric emissions from the photovoltaics industry, and, since the quantities of pollutants are relatively small, is unlikely to do so.

State environmental protection agencies, however, also regulate hazardous emissions from industrial sources. In New York State, for example, the Department of Environmental Conservation (NYSDEC) air pollution control engineers use threshold limit values to derive Acceptable Ambient Levels (AALs) and have established control and monitoring requirements for toxic gases. They evaluate potential air quality effects by calculating an expected maximum ambient concentration (MAC) from emission flow rate, stack height, and TLV concentration, according to the empirical formula applicable for all gases:

$$\text{MAC } (\mu\text{g/m}^3 = \frac{\text{emission rate (lb/hr)} * 4218}{[\text{emission height (ft)}]^{2.16}} .$$

An MAC is considered safe if it does not exceed a fraction of the material's TLV. The safety factor is 1/300 for PH_3 and other high-toxicity pollutants and 1/50 for low- or medium-toxicity pollutants [8]. Safety factors are in general applied because the IDLH was derived for the control of workers' exposure and was not intended to be used to assess the effects of exposure of the general public. The working population is more healthy and resilient than the total population, which includes very young, very old, and infirm members.

Other regional agencies also may require industry to follow certain practices in handling, storing, and monitoring hazardous materials. Two fires involving hazardous materials that happened in late 1979 and early 1980 in Silicon Valley, California semiconductor facilities, for example, have led to the establishment of an integrated management and emergency response plan for Santa Clara County which requires all industries to report inventories of hazardous materials and to implement spill-monitoring and safe-storage programs. On January 1, 1984 a modified version of this plan became a state law in California [9].

At present there are no federal regulations aimed at preventing the accidental release of hazardous substances from manufacturing or chemical plants. Hazards from accidental material releases in manufacturing or chemical plants are not yet directly regulated by any federal agency and the burden to protect public health falls on industry. There are federal regulations aimed at reducing the likelihood of accidental release of hazardous materials from commercial nuclear power plants, offshore oil and gas facilities, hazardous materials pipelines, and liquified natural gas facilities [10]. These include requirements for safety equipment, training, record-keeping, and emergency planning. Federal involvement in each of the regulated industries includes data collection, research on safety standards and technology, establishment of standards, inspections, and enforcement. The safety regulations incorporate to some extent standards developed by industry. The tragedy in Bhopal, India has raised concerns about safety in the chemical industry. EPA and the United Nations International Labor Office (UN-ILO) have produced interim lists of toxic chemicals that may present serious health risks from short-term exposures during accidental release [11], and estimates of dangerous quantities of these materials. Both lists include phosphine. Phosphine potentially dangerous quantities from these lists are compared with the weekly required quantities at a 10 MWp/yr photovoltaic cell factory (Table 1).

Table 1. Comparison of phosphine inventories with threshold limit quantities

	Use[a] (kg)		Threshold storage quantity (kg)	
Source	Annual	Weekly	US-EPA[b]	UN-ILO[c]
Zn_3P_2 - MOCVD[d]	4000	80	150	100
a-Si CVD[e]	2	0.04	150	100

[a] For a plant with a yearly production of PV cells capable of generating 10 MWp [1,2].

[b] Quantity identified by the US-EPA which if released could present an acutely toxic exposure beyond 500 m from the source.

[c] Limits of stored quantities, as defined by UN-ILO; larger-than-limit quantities may present major accident hazards.

[d] Metallorganic chemical vapor detpostion.

[e] Chemical vapor deposition.

4 AIR POLLUTION CONTROL SYSTEMS

Release of PH_3 to the environment may pose health risks to communities near photovoltaic plants. Release may be either from venting of effluent gases from process and control equipment, or from leaks in process and gas systems. Methods for removing PH_3 from emissions include wet scrubbing, carbon adsorption, and thermal oxidation.

4.1 Wet Scrubbing

Wet scrubbing with potassium permanganate ($KMnO_4$) or sodium hypochlorite/sodium hydroxide (NaOCl/NaOH) solutions is a common method for controlling small quantities of PH_3. Packed-tower scrubbers bring gas and scrubbing liquid in contact countercurrently, but have the limitation that plugging may occur when large quantities of "sticky" particulates are produced. In a basic spray-type scrubber, gas enters an expansion space where its velocity is reduced and it passes slowly through scrubbing liquid sprays, but this design is not effective at high gas-flow rates. A variation of the spray scrubber is the venturi scrubber, in which gas is accelerated by passing through a small opening into a converging nozzle. The high velocity of gas and the injection of scrubbing liquid create high turbulence and good mixing of liquid and gas. Venturi scrubbers are efficient in collecting fine particulates while cleaning up gaseous pollutants, but their efficiency is very sensitive to pressure drops; for varying flow rates, an adjustable-throat opening is required. Venturis are used more frequently for small, variable, or intermittent gas flows.

Combinations of scrubbing methods may result in higher removal efficiencies. Venturi and packed-bed scrubbers used in sequence can effectively control PH_3 streams. Experiments on controlling AsH_3 (a gas chemically comparable with PH_3) with $KMnO_4$ have shown packed-tower efficiencies of 80% to >99% for concentrations of 20 ppm AsH_3 at an air-flow rate of 2.4 lb/hr [13], but treatment of the scrubbing solution for recycling or discharge has proved to be a more difficult technical problem. $KMnO_4$ reacts with PH_3 according to the reactions:

$$4PH_3 + 6KMnO_4 \longrightarrow 3Mn_2O_3 + 2K_2HPO_3 + 2KH_2PO_3 + 3H_2O \ ,$$

$$3PH_3 + 6KMnO_4 \longrightarrow 3K_2HPO_3 + 3H_2O + 6MnO_2 \ .$$

Accumulation of manganese oxides produces foam and sludge that can plug the scrubber, but antifoaming agents can be added, and precipitates can be removed with 5% sodium bisulfite solution.

Adsorbed and oxidized components must be removed from the permanganate solution before recycling or discharge. Experimental work on AsH_3 control has shown that ferric sulfate added to scrubber liquor removed 90% of the arsenic with minimum permanganate loss and sludge generation [13]. Normal operation would require daily bleeding to prevent excessive accumulation of manganese oxides and other solids and to maintain the permanganate concentration in the recycled liquor. Bleed solution can be stored and treated with ferric sulfate and sodium hydroxide on, for example, a weekly batch basis. The permanganate filtrate would be recycled. This method of cleaning scrubber liquor in the storage tank for recycling can be used also in PH_3 scrubbing. Spent scrubber liquor, which eventually must be discharged, may need further treatment with sodium bisulfite and lime to meet effluent standards for phosphorus and manganese.

In a H_2 environment (e.g., MOCVD of Zn_3P_2), potassium permanganate should not be used because it can react violently with H_2 to produce a fire or explosion; therefore, NaOCl is preferred. This produces smaller quantities of sludge than does $KMnO_4$, but it attaches strongly to metal surfaces and requires very accurate control of the alkaline environment.

4.1.1 Control Costs

The annual production of Zn_3P_2 photovoltaic cells by metallorganic chemical vapor deposition, capable of generating 10 MWp, is estimated to require 4027 kg PH_3 a year [2]. Assuming a 30% process efficiency, about 3050 kg PH_3 remaining unreacted will require treatment before release to the environment. PH_3 gas can be chemically inactivated with $KMnO_4$ in a venturi scrubber; 3050 kg PH_3 will require about 216,000 kg $KMnO_4$, at an approximate cost of $431,000 [2]. The capital cost of the scrubber and accessories is about $15,000, and the annual operating and maintenance cost is about $900 (6% of capital cost) [2]; for these, the total annualized cost is 4.3¢ per Wp of PV cell generating capacity produced.

4.2 Carbon Adsorption

Carbon adsorption is very effective in removing PH_3 from an effluent stream of moderate flow rate and low concentration [11-13]. Experiments comparing $KMnO_4$ wet scrubbing and carbon adsorption for AsH_3 control in air streams of 20 ppm AsH_3 showed carbon adsorption to have the advantages of lower cost, simpler operation, and fewer waste disposal problems [13]. The carbon was a type impregnated with copper and chromium oxide (Type FCA), which has shown higher arsine-absorbing capacity than several other adsorbents. Porous carbon adsorbs phosphine molecules by mechanisms involving Van der Waals surface attraction and capillary condensation, and its capacity depends on its properties and on the operating conditions. The same type of carbon, used for PH_3 removal [14,15] in systems with total flows up to 100 cfm, has shown about 10% wt loading capacity [15]. This indicates that carbon adsorption may be very effective in controlling PH_3 at the very low flow rates used in some photovoltaic industries (e.g., a-Si), but not at the high flow rates of routine emissions or potential accidental releases of a 10 MWp Zn_3P_2 photovoltaic cell plant. In these cases, high temperatures generated in the bed, will make it ineffective.

The economics of a carbon adsorption system have not been examined, but it may provide an economically plausible method of PH_3 recovery. PH_3 can be regenerated from carbon by heating with steam or hot air, either internally with a fixed bed or externally with a moving bed. PH_3 regeneration is not practiced in today's small applications; the drums of saturated carbon are closed and sent to landfills. Any regeneration or disposal methods will have to be examined in relation to applicable emission controls.

4.3 Thermal Oxidation and Combustion

Control of combustible PH_3 streams by thermal oxidation or incineration is economically favored when the generated heat can be put to use. In an emergency, incineration may create explosion hazards, and its efficiency in removing toxic gases may be lower than those of the other methods. Safety and insurance regulations normally limit the maximum concentration of a controlled gas to 25% of the low explosion limit. This concentration will supply only part of the heat required to sustain combustion so that auxiliary fuel may be needed.

A combustion/oxidation system which is highly efficient for the removal of silane and diborane has been found inefficient in controlling phosphine [16]. This system operated at 800°C to 1000°C and higher temperatures may be required for phosphine. Another system proposed to control accidental releases of phosphine is the Dynacycle [17], in which PH_3 is burned with air in a stand-by diesel generator. When a leak is detected in a process or storage system, the leaking PH_3 is automatically directed through duct works to a diesel generator, where the PH_3 thermally oxidizes to less hazardous solid materials. The solids are removed by filtration, and the filtered diesel exhaust is diluted with air before release. Preliminary tests by the manufacturer on a small (2.5-kW) diesel indicated that the diesel engine, operating as a thermal oxidation unit, can remove more than 99% of the PH_3 in the air it consumes [17]. These tests were done with 0.2% PH_3 in hydrogen, and with pure PH_3 diluted with argon to below its low explosion limit. The Dynacycle system has yet to be tried in larger applications. A full cylinder leak may discharge about 4200 l/min of 100% PH_3 (worst case) within 5 minutes. In this case, use of a 100-kW diesel generator capable of consuming about 4200 l/min of air is suggested [17]. The costs of these systems have not been examined.

5 ROUTINE GAS RELEASES

Estimates of quantities of pollutant effluents from normal operation, with and without controls, presented in earlier studies [1,2] are summarized

Table 2. Phosphine emissions from thin-film photovoltaic cell plants

Source	Emissions (lb/hr)* Uncontrolled	Emissions (lb/hr)* Controlled**
Zn_3P_2-MOCVD***	$7.8x10^{-1}$	$4x10^{-2}$
a-Si glow discharge	$1x10^{-4}$	$6x10^{-6}$
a-Si reactive sputtering	$1x10^{-4}$	$6x10^{-6}$
a-Si chemical vapor deposition	$3x10^{-4}$	$1.5x10^{-5}$

*Plant operating 24 hr/day, 350 days/yr, with annual production of PV cells generating 10 MWp.
**Based on 95% scrubber efficiency, with NaOCl/KOH scrubber.
***MOCVD = Metal organic chemical vapor deposition.

in Table 2. In plants where PH_3 is used only as a dopant gas, (e.g., a-Si processes), only minute quantities (0.5 to 1 cm^3/min for a 10 MWp/yr plant) of PH_3 are expected in the effluent streams [1]. In the same size Zn_3P_2 plants, however, much larger quantities (about 4 l/min of 100% PH_3 equivalent) are expected [2].

It appears that wet scrubbing, possibly with carbon adsorption as final control, currently provides the most efficient and safe phosphine control. Commercially available multistage scrubbers are about 95% efficient in removing these pollutants. Assuming 95% removal, PH_3 emissions from such a Zn_3P_2 plant will be only about 80 cm^3/min, and those from plants using PH_3 only as dopant gas should be below detectable limits.

Analysis using the screening method of the New York State Department of Environmental Conservation (see Section 3.2) suggests that routine emissions from both a-Si and Zn_3P_2 10 MWp/yr plants will produce ambient concentrations well below the threshold limit value fraction, at any time (Table 3). Consequently, routine emissions should not endanger public health.

Table 3. Ground-level concentrations of PH_3 during normal operation

Source	Emission rate* (lb/hr)	Maximum concentration (mg/m^3)**	Maximum concentration % of TLV***
Zn_3P_2 - MOCVD	4×10^{-2}	2×10^{-4}	0.05
a-Si glow discharge	6×10^{-6}	2×10^{-8}	5×10^{-6}
a-Si reactive sputtering	6×10^{-6}	2×10^{-8}	5×10^{-6}
a-Si chemical-vapor deposition	1.5×10^{-5}	6×10^{-8}	2×10^{-5}

*Based on 95% scrubber efficiency.
**Estimated by the NYSDEC procedure, assuming an emission height of 25 ft.
***The PH_3 threshold limit value (TLV) is 0.4 mg/m^3.

6 ACCIDENTAL GAS RELEASES

In the U.S., most major incidents in which toxic gases and vapors have caused fatalities involved releases into the environment of chlorine or ammonia from rail and road tankers, pipelines, storage tanks, etc. [18], in amounts measured in tons. In contrast, PH_3 is normally used and stored in much smaller quantities and thus presents much smaller hazards -- of course, the "catastrophic" potential depends not only on the quantity of a gas released, but also on its toxicity.

6.1 Gas Systems

Gas systems in photovoltaic cell manufacturing plants include source, distribution, point-of-use, and exhaust subsystems. The source subsystem consists of cylinders, valves, regulators, cylinder purge assemblies, filters, etc. The distribution subsystem used to transport gases from remote storage areas to process equipment comprises pipes, fittings and joints, in-line shut-off valves, and pressure gauges or transducers. The point-of-use subsystem includes valves, regulators, and piping connected with the process deposition system. The process deposition and exhaust systems include pumps and piping.

The distribution and point-of-use subsystems may require limited worker interface and are usually fixed. The gas source subsystem is active in comparison, being subject to more frequent changes (e.g., cylinder changes).

Deposition takes place via glow discharge, reactive deposition, or heating, in chambers kept at reduced pressure, from which excess reactant gases and by-products are removed by vacuum pumps that compress them from a few torr to atmospheric pressure. In all process operations, worker interface with process equipment, gas distribution, point-of-use, and exhaust systems can be limited. Transfer of substrates through the deposition chambers as well as process control and monitoring can be done remotely from a control room.

6.1.1 Leakage

Some parts of gas systems, such as connections, valves, and pumps, are more susceptible to leakage than others. Leakage prevention requires not only good design but also detection and repair programs [19]. Phosphine is usually used in low-pressure deposition systems that include pumps, connections, traps, chambers, and load-locks. Accidental entrance of air may cause a fire or explosion.

6.1.2 Vacuum Pumps

Vacuum pumps can leak through junction seals and valve stem seals. Eliminating the gas ballast valve or connecting it to a dry-nitrogen line will prevent air from accidentally entering the vacuum system. Contamination of pump oil by PH_3 or reaction by-products presents potential health and safety hazards since the PH_3 in the pump oil may later escape into the air. Contaminated pump oil should be stored in closed vessels in well ventilated areas. The introduction of purging nitrogen gas through the oil might be advantageous, to create bubbles that continuously clean the oil bath. Nitrogen bleeding is also desirable to prevent oil back-streaming. Most mechanical pumps require frequent maintenance. Abrasive particles (e.g., Si) passing through the pump cause degradation of bearings and seals on revolving shafts and eventual leakage and should be traped in an oil filtration system. Filters, oil bearings, and seals should be periodically inspected. Exhaust gases from the pumps are either scrubbed or vented safely. Oil-free vacuum pump exhaust filters can be used to eliminate duct fire hazards caused by oil and to protect scrubbers from oil contamination; they can also recover expensive lubricants.

6.1.3 Gas Systems Purging

During replacement of PH_3 cylinders and during maintenance work on gas systems, workers may be exposed to health and safety hazards if gas trapped in a line escapes to the air. Such hazards can be minimized by purging the system before starting work. Purging is accomplished either by evacuation or by replacing PH_3 with inert gas, or by a combination of the two. Evacuation has the drawbacks that it takes a long time and it cannot remove all gas; it is therefore normally used only in conjunction with replacement. The two common replacement methods are continuous-flow purging and cycle purging. In simple systems such as tubing, continuous purging is effective although it takes a long time to attain very low concentrations, but in systems with branches and dead-end cavities such as a regulator assembly, cycle purging is far more effective because continuous purging does not adequately purge dead volumes. Cycle purging comprises introduction of purge gas into a system (pressurization) and release of the mixture of purge gas and undesired gas from the system (venting). Before changing cylinders the regulator is pressurized with an inert gas through the purge assembly, and then it is vented to atmospheric or lower pressure with a vacuum pump. Purging efficiency is increased by increasing the number of cycles and the purge gas inlet pressure and reducing the venting pressure, according to the formula

$$C_n = \left(\frac{Po}{P_o + P} C_o \right)^n$$

where C_n is the gas concentration after n cycles; Co, the initial gas concentration; P_o, the venting-down pressure; and P, the pressure of the inert gas during pressurizing. Purging efficiency can be further improved by designing gas systems with limited numbers of branches and dead-end cavities and by isolating the necessary branches (e.g., pressure gauges) from spaces that require frequent purging.

The purge system includes a flow-limiting purge valve, vent check, diaphragm valves, pressure regulator, and vacuum pump. The flow-limiting valve provides automatic shut-off in case of excessive flow due to a leak anywhere in the system. The purge and vent valves are button activated and provide a momentary flow passage while assuring that the flow will be shut off when the manual action stops. During purging the pressure regulator is tightly sealed by diaphragm valves in its inlet and outlet. A check valve in the line connecting the purge supply to the gas supply prevents the gas from entering the purge line. Pressure regulators designed to handle corrosive gases include a valve seat assembly attached to the diaphragm component to provide back-up for shut-off if the normal regulator fails. Such regulators made by several manufacturers [e.g., 20-22] operate at pressures from vacuum up to 3000 psi and temperatures from -40°F to +2000°F without diaphragm distortion or seal deterioration.

Remotely controlled purge systems can further enhance occupational health and safety. They consist of two units: the automatic remote-control assembly located outside the gas storage cabinet, and the purging manifold connected to the gas cylinder. The automatic controller provides essential safety features such as automatic shut-off of gas delivery to the process in the absence of purge gas supply, remote control of purging operations, and warning signals in the event of system malfunctioning, leak, or shut-off.

6.2 Preventive Options

Passive options aimed at preventing rather than controlling PH_3 gas leakage probably provide the best approach to the accidental release problem. These include flow-restricting orifices in cylinders, safety excess-flow valves, heat-resistant cylinders and covers, and others. In an accident flow-restricting orifices and valves may reduce catastrophic instantaneous release of a cylinder's contents to release over a longer time at lower flow rate. Active controls (e.g., stand-by scrubber) are certainly more effective at lower flow rates, and longer release times for a given mass allow enhanced atmospheric dispersion and more time for emergency response.

6.2.1 Cylinders

For safety, stainless steel cylinders are preferred to aluminum cylinders because of their mechanical strength over a range of stress conditions. Steel can sustain temperatures above 1000°F without significant loss of mechanical strength. Aluminum cylinders offer certain technical advantages for PH_3 applications, but they show substantial loss of mechanical strength when exposed to heat, severe enough above 450^{o}F to result in failure. Stronger aluminum cylinder packages such as Linde Fibralume [23] reduce cylinder failure risks. Fibralume is a carbon-fiber composite cylinder overwrap to insulate and protect the cylinder's sidewall from accidental exposure to heat, with special resin bonded into it that permanently changes color when exposed to dangerous heat levels to warn that the cylinder may have been weakened and must be taken out of service.

6.2.2 Valves

Valves designed for safety may include one or more of the following features: remote control, flow restriction, automatic shut-off upon warning signal, and shut-off within the cylinder. Remote-controlled cylinder valves can reduce potential hazards associated with handling highly toxic gases such as PH_3. A recently introduced valve [23] features pneumatic operation that permits opening and closing of the valve from a remote location, pressure reduction to 1000 psi, flow restriction in the event of downstream leak, and secondary sealing that prevents leakage to the atmosphere if the primary seal leaks or the valve is inadvertently opened. The valve is supplied together with the cylinder at a rental cost of ~$30/month. Remote-controlled valves can be operated by electronic signaling from toxic gas monitors. Flow-limiting/safety shut-off valves automatically stop the flow in a line when flow exceeds a factory pre-set level. The flow-limiting valve is normally installed between the cylinder outlet and the pressure regulator inlet, to enhance safety in this high pressure area of the system. Another type of flow-limiting valve, designed to be inserted in the low pressure delivery line from the process regulator to the process, automatically shuts off the gas supply if the flow exceeds a pre-set limit. A valve being developed by the Veriflo Corporation [20] is built within the cylinder, is remotely operated and, in connection with suitable monitors, automatically closes at the cylinder in the event of excess flow.

There are also types of safety excess-flow valves that can be intersected anywhere in a gas system which instantly stop excess gas flow caused by a broken tube or fitting.

6.2.3 Valve Connections

Since valve connections are often subject to leakage, new types may be required for PH_3 gas. They should be made of stainless steel, be helium tight (leakage rate $<10^{-8}$ cm^3/min), and should have flow-reducing orifices. A Semiconductor Equipment and Materials Institute (SEMI) cylinder-valve task force has recommended that, in addition, they should be operational over a temperature range of -40°F to 325°F, be distinguishable from other valve connections, withstand abuse, and include an outlet plug that can withstand full cylinder pressure.

6.2.4 Monitoring Systems

Commercially available monitors that can detect very low concentrations of PH_3 in a short time (Table 4) should be used for early detection of PH_3 leaks. They respond to PH_3 at the TLV level (0.3 ppm) in a few minutes, and to higher concentrations in a shorter time (e.g., 40 sec to detect 12 ppm). They are based on photo-absorption or photoionization and consist of PH_3-adsorbing medium, a light source, and a photo cell or ionization sensor. A monitor continuously drawns in ambient air by a low pressure vacuum pump, analyzes it, and displays the results. A pre-set trigger-level concentration sets off both visual and acoustic warnings. Some systems offer the option of remote alarm/documentation stations located

Table 4. Phosphine detection systems

Operation principle	Model	Type	Low detection limit (ppm)	Response time at TLV (0.3 ppm)	Cost ($)
Photo-absorption	MDA, Series 7100	Single-point	0.05	10 sec	~ 7,500
	PSM-8[24]	Multipoint	0.01	10 sec	>26,000
	Matheson, Model 8040[22]	Single-point	0.05	10 min	~ 7,500
Photo-ionization	Airco[25]	Single-point	0.02	30-90 sec	*
	Telos Labs, Model 650[17]	Multipoint	0.01	8 sec	*
Thermal conductivity	Matheson[22]	Portable	0.13	*	*
Color change	SKC[26]	Portable	0.1	*	~300
	Sensidyne[27]	Portable	0.15	<30 sec	*
FT-IR	Telos Labs, ACM[17]	Multipoint	*	*	*
Flame photometry	CEA Industries, Model 578[28]	Multipoint	0.001	20 sec	>32,000
Electro-chemical cell	Sensidyne[27]	Portable, micro-processor control	0.1	<30 sec	*
	Gas Tech[29]		*	*	

*Not reported.

far from the monitor; this improves personnel response time and functioning during an emergency.

Single-point monitors are commonly used to detect potential leaks in storage cabinets. Separate monitors are then used to measure concentrations in other places; these can keep potentially hazardous areas under constant surveillance and can be connected to alarm, ventilation, and control systems. Multipoint monitors can continuously measure PH_3 concentrations in eight or more locations. These are microprocessor-controlled systems and can be programmed so that alarm levels, sampling sequence, and monitoring frequency can be adjusted. When alarm-triggering conditions occur, the systems present the location of the leak, document it, and activate the appropriate alarm relays. All these detectors can detect PH_3 and several also detect other hydride gases. These systems can document concentrations on a minute-by-minute, point-by-point basis and/or document the accumulated 8-hr time weighted average for each individual monitoring point. Documentation can be transmitted to control rooms or other remote locations with an optional remote alarm/documentation station.

Photoionization systems are of higher sensitivity than other systems. A monitoring system based on a photoionization sensor and a microprocessor-controlled gas chromatograph is claimed to have a sensitivity in parts per billion (ppb) for PH_3 [25]. It has two distinct modes of operation, quick-scan and analytical. The quick-scan mode provides fast response to a leak in up to ten source channels. If the system detects dangerous concentrations due to a leak, it automatically switches to the analytical mode, in which a gas chromatograph is used to provide accurate PH_3 concentration levels and activate warning systems.

Systems of high sensitivity that can measure hundreds of compounds are based on Fourier-Transform Infrared (FT-IR) analysis. These monitoring systems can quickly detect very low concentrations of PH_3. They are designed so that failure of one or more components produces an alarm sound.

Positioning of the monitor sampling points is important for occupational safety. They should be as close as possible to sources of leaks and away from places where ventilation draft may dilute or recirculate the leaking gas. Commercially available personal lightweight portable monitors can provide visual or audible warning to employees who work in or enter potentially hazardous environments.

6.3 Control Options

Options for controlling massive releases of PH_3 gas in the atmosphere are known, but their effectiveness in emergency situations has not been demonstrated. The following criteria should apply in designing any system for controlling accidental release:

(i) The system should be mechanically simple; it should have few if any moving parts and a minimum number of connections and seals.

(ii) Fail-safe operation should be assured to the highest degree possible (e.g., operation on tap water pressure in the event of power failure, back-up power).

(iii) Given the uncertainty of release conditions, the system should operate under a wide range of flow rates.

Chemical spray scrubbers can be designed and sized to handle limited massive releases, but the above criteria may exclude designs with variable-flow orifices, many buffers, and packed towers. A simple batch-operated spray scrubber, in which the released gas is entrained and subsequently inactivated by repeated scrubbing in a recirculating system, may control gas releases under a wide range of release conditions; it would be sized to handle a "worst reasonable" release case.

Thermal oxidation systems such as the Dynacycle described in Section 4.3, may also be reliable in emergency situations since they can handle high flow rates of gas.

6.4 Atmospheric Dispersion

Integral to effective emergency planning and response is the ability of plant safety managers to predict the location, concentration, and size of gas clouds resulting from accidental release of hazardous compounds. Quick and accurate prediction of the consequences of a given release will be required in emergencies to allow decisions about protecting plant personnel and neighboring populations. This involves evaluation of the following:

(i) initial formation of a cloud;

(ii) cloud dispersion to the point where it ceases to present a hazard (i.e., to the point where PH_3 concentration drops to the critical concentration level);

(iii) health impacts if the cloud passes over a population, or if it is ignited.

6.4.1 Formation Phase

In the cloud formation phase the "source" term is determined. It depends on the quantity of gas (for a sudden release) or the rate of gas release (for a relatively continuous release) and on the geometry of the source. However, for the examined point releases, dispersion is not very sensitive to the source geometry. Source geometry variations influence the mass of air entrained, but do not significantly affect the results for distance over which the cloud is hazardous. This is because an increase of the initial volume of a specific mass release is accompanied by a reduction in mixing produced by gravity spreading, counter-balancing the advantage of the lower dilution factor necessary to achieve the desired reduction in concentration: the total negative buoyancy of the initial cloud is the important factor, and it is independent of the initial dilution. In contrast, the results for flammable gas dispersion depend critically on the assumptions for mass of air entrained and initial geometry of the cloud.

6.4.2 Dispersion Phase

In the dispersion phase the source data are used in combination with meteorological data, and sometimes terrain shape data, in atmospheric dispersion models to calculate transport and dispersion of released gases. Dispersion models determine the concentration at any position downwind by considering the time passed after the "puff" release, diffusion in the downwind direction, and lateral and vertical diffusion. The path of the "puff" is difficult to simulate but, assuming that the puff travels in a "straight line" in the direction of the prevailing wind, the concentration for a particular downwind distance or travel time can be determined by using a Gaussian puff equation of the form:

$$C(x,y,o,h) = (2Q/(2\pi)^{3/2} \sigma x \sigma y \sigma x) \exp[-0.5(x - ut)]$$

σx is the standard deviation of the concentration distribution in the downwind direction, and t is time elapsed after release. According to this formula there is no dilution in the downwind direction. The wind speed (u) serves mainly to give the downwind position of the puff. Wind speed may influence the dispersion indirectly because the dispersion parameters may be functions of wind speed. Estimates of the dispersion parameters are presented in several texts [e.g., 30,31]. Atmospheric dispersion calculations using a Gaussian plume model [32] show that large areas will be affected if the quantities shown (Table 5) are accidentally released in the atmosphere in a very short time (e.g., 5 min).

The terrain around a photovoltaic cell facility may influence the dispersion potential of released gases and hence the associated hazard. During periods of low winds and stable atmospheres, the heavier-than-air gas

Table 5. Ground-level concentrations of PH_3 from accidental instantaneous release with weather pattern assumed stable

Source	Quantity released (lb)	Distance downwind (m) to 200 ppm[1]	Distance downwind (m) to 0.7 ppm[2]
Zn_3P_2 - MOCVD	26	250	1500
	170	450	2800
a-Si doping	0.2	40	300

[1] 200 ppm is the (IDLH) concentration defined in Section 3.1.
[2] 0.7 ppm assumes a safety factor of 1/300 applied to IDLH.

Note: Ground concentrations derived from the dispersion model were estimated as time-averages over 30 min to allow comparison with the IDLH limit of exposure.

may flow into and be trapped in ravines, presenting increased hazards to populations living there. The most stable atmospheres occur during nighttime inversions and, along with drainage winds and high relative humidity, present the worst atmospheric dispersion conditions. In an emergency situation, meteorological data in the form of stability classes, mixing height, and wind speed and direction can be readily used. Complex wind patterns and complex terrain data may not be available, however; information about terrain effects on dispersion, collected in advance, can be used for more accurate prediction of toxic gas concentrations outside a plant. Collection of such information requires techniques such as monitoring of tracer-gas release and remote sensing, with lidars, of clouds resulting from a release.

Atmospheric dispersion programs can be implemented on microcomputers for use by emergency response teams, state agencies, and industrial facilities. Useful outputs include isopleths defining the physical bounds of a dispersing cloud on the basis of preselected concentration levels (e.g., IDLH). These are helpful for rapid assessment of the atmospheric dispersion of the toxic material and estimation of the population at risk.

6.4.3 Health Impacts

Health and air quality impacts of phosphine clouds passing over a populated area depend on the resulting ground-level concentrations and on the duration of exposure. The IDLH level is a reasonable measure with which to compare estimated concentrations resulting from instantaneous releases because the residence time of the cloud over any given location is relatively short. Furthermore, a safety factor of at least 1/100 should be applied since the IDLH concentration is for healthy workers and not for the general population, which includes many very young, very old, or infirm members.

6.5 Emergency Preparedness and Response

Accidental release of PH_3 gas may pose an immediate threat to the nearby population or operating personnel. Given the uncertainty in the effectiveness of large-release control options, investing in systems to prevent or minimize release is preferable to investing in release control options. Nevertheless, a release may happen despite preventive measures. Response to a release can be greatly improved by planning in advance how to minimize impacts and by training plant, fire department, police, and medical personnel in proper response procedures. Lack of emergency preparedness can increase the risk to occupational and public health.

6.5.1 Federal Plans

Currently there are no federal requirements for chemical or semiconductor plants to develop off-site plans for protecting the public in the event of an emergency. EPA has recently announced a Chemical Emergency

Preparedness Program for dealing with accidental releases of acutely toxic hazards. This program has two goals: (i) to increase community awareness of chemical hazards, and (ii) to develop state and local emergency response plans for dealing with chemical accidents. It gives recommendations on (i) how communities can organize to develop plans, (ii) how information on toxic chemicals, associated risks, control measures, and emergency plans can be gathered from local facilities, and (iii) how this information can be used to develop community contingency plans.

6.5.2 Industry Plans

Industry's self-interest provides the willingness and capability to prevent accidents. There is much concern and activity underway within the chemical industry to evaluate and upgrade its safety systems. Chemical and semiconductor plants generally have plans and procedures for handling in-plant incidents such as spills and fires. The semiconductor and consequently the photovoltaic cell industry will undoubtedly benefit from the chemical industry's efforts in the gas safety area.

Recently, in response to the accident at Bhopal in 1985, the chemical industry has undertaken several activities to prevent similar accidents from happening elsewhere. These include the establishment of two chemical institutes and the emergency program of the Chemical Manufacturers Association (CMA). The chemical institutes are the Center for Chemical Plant Safety, being established by the American Institute of Chemical Engineers (AIChE), and the National Institute for Chemical Studies, to be established in West Virginia with joint funding from the State of West Virginia and the chemical industry [10,33]. The Center for Chemical Plant Safety will examine safety issues including release of toxic materials, and it will also make recommendations on new technologies that industry can use to develop safer processes. The CMA program includes an expanded emergency response training program to train industry emergency personnel and to develop emergency training information for police, fire, and other emergency response personnel. Another CMA initiative is the Community Awareness and Emergency Response (CAER) project. As part of the project's activities CMA has prepared a handbook to assist companies in developing community awareness programs and plant and local emergency planning [34]. CAER'S overall goal is (i) to provide information to the public on hazardous chemicals, (ii) to review, renew, or establish emergency response plans, (iii) to expand the industry's involvement in community response planning and emergency networks, and (iv) to initiate integrated community emergency response planning.

6.5.3 Local and Regional Agency Plans

Many regional and local agencies have general emergency plans for a variety of disasters. An example is the integrated management and emergency response plan for Santa Clara County [9], aimed at preventing disasters from hazardous materials used in the semiconductor industry. This plan was drafted by fire department personnel, chemists, engineers, environmentalists, lawyers, industry and labor representatives, and risk management officials. In chemical plants, managers have in several cases assisted in integrating chemical plant accident procedures with community plans. No comprehensive assessment is known to have been made by industry or government on the number or status of such plans. Emergency preparedness plans probably vary from plant to plant. The federal government would directly respond to a toxic gas release emergency only in a situation in which the capabilities of state and local authorities or other responsible parties were exceeded; the EPA and the Federal Emergency Management Agency

(FEMA) would likely be the major federal agencies in such a situation. Risks due to potential releases of PH_3 gas from photovoltaic cell facilities are such that emergency procedures can probably be handled by local authorities, but the EPA can assist local agencies by conducting training programs and encouraging integration of government and industry safety initiatives.

7 DISCUSSION

Phosphine gas used in the production of thin-film photovoltaic cells can present serious public and occupational health risks, if appropriate prevention and control options are not effectively implemented. Quantities of PH_3 used for doping are small; existing controls can effectively minimize potential health risks when only small quantities are present at the manufacturing facility. Use of the gas in the production of Zn_3P_2 photovoltaic cells presents added risk to public and occupational health. Most serious accidents will probably result from leakage of stored material. Atmospheric dispersion calculations suggest that this could jeopardize life and health of populations living near these plants. Accident prevention or minimization options, such as flow-restricting valves, monitoring systems, and fire-resistant cylinders, need to be implemented to reduce this hazard. A flow-restricting valve, for example, may reduce rates of flow from a leaking vessel to levels manageable for a scrubber and give more time for emergency response. Nevertheless, given the size of the potential hazard, both preventive and control engineering systems, as well as emergency preparedness and response plans will be needed. A complete control cost analysis has not been done, but preliminary cost estimates of the chemical scrubber show a relatively high control cost [2]: 4.3¢ per Wp for the scrubber which is only a part of a total control system.

Phospine used as a dopant is present in low quantities that do not represent extraordinary hazards; preventive and control options can effectively minimize risks, and use of lower pressures and concentrations can further enhance safety.

The feasibility of substituting other feedstock materials for PH_3 needs to be examined: the best way to prevent leakage of a hazardous material is to replace it with a less hazardous material. Solid Zn_3P_2 can substitute for PH_3 in the production of Zn_3P_2 photovoltaic cells if closed-space vapor transport deposition is used instead of metallorganic chemical vapor deposition. Zn_3P_2 is also highly toxic, but being a solid, it can be safely stored and does not present the hazard of accidental leakage. The material as currently being produced could easily be scaled-up to meet the material needs of deploying Zn_3P_2 photovoltaic cells capable of generating 25 GWp [35].

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