U.S. CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD

INVESTIGATION REPORT

CHLORINE RELEASE

(16 Medically Evaluated, Community Evacuated)

DPC ENTERPRISES, L.P.

GLENDALE, ARIZONA

NOVEMBER 17, 2003

KEY ISSUES:

- MATCHING SAFEGUARDS TO RISK
- OPERATING PROCEDURES
- REACTIVE HAZARDS
- EMERGENCY RESPONSE

REPORT NO. 2004-02-I-AZ

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Contents

Figures

Tables

Acronyms and Abbreviations

AIChE	American Institute of Chemical Engineers
CCPS	Center for Chemical Process Safety
CFR	Code of Federal Regulations
CSB	U.S. Chemical Safety and Hazard Investigation Board
EPA	U.S. Environmental Protection Agency
EPCRA	Emergency Planning and Community Right-to-Know Act
ERPG	Emergency Response Planning Guideline
HAP	Hazardous Air Pollutant
IDLH	Immediately Dangerous to Life or Health
mV	Millivolts
NIOSH	National Institute for Occupational Safety and Health
OSHA	Occupational Safety and Health Administration
ORP	Oxidation Reduction Potential
PEL	Permissible Exposure Limit
PHA	Process Hazard Analysis
PPE	Personal Protective Equipment
ppm	parts per million
psi	pounds per square inch
PSM	Process Safety Management (OSHA)
RMP	Risk Management Program (EPA)
REL	Recommended Exposure Limit
STEL	Short-Term Exposure Limit
vSMS	Voluntary Safety Management System

EXECUTIVE SUMMARY

On November 17, 2003, a chlorine gas release at DPC Enterprises (DPC) in Glendale, Arizona, led to the evacuation of 1.5 square miles of Glendale and Phoenix. Five residents and 11 police officers sought medical attention for symptoms of chlorine exposure and were treated and released.

The DPC Enterprises facility in Glendale repackages chlorine from railcars into smaller containers. DPC captures chlorine vented from these operations in one of two caustic scrubbers that also produce household bleach for sale as a byproduct.

The U.S. Chemical Safety and Hazard Investigation Board (CSB) determined that excess chlorine vented to the scrubber, where it completely depleted the active scrubbing material (caustic) and over-chlorinated the scrubber. The resulting bleach decomposition reaction released a cloud of toxic gases into the surrounding community. Emissions continued at a decreasing rate for about six hours. The incident ended when workers injected additional caustic into the scrubber to stop the decomposition reaction.

The CSB investigation identified the following root cause:

- The single, procedural safeguard provided by DPC was not commensurate with the risk of over-chlorinating the scrubber. Additional safeguards should have been in place to prevent or mitigate scrubber over-chlorination, such as automatic shut-off of chlorine prior to over-chlorination, automatic or remote caustic injection to interrupt the decomposition reaction, or a downstream (secondary) scrubber to treat emissions from the over-chlorinated scrubber.

The CSB investigation identified the following contributing causes:

- Contrary to procedure, practice at the DPC site was to continue chlorine flow to the scrubber during quality control testing. Management did not detect this deviation.

- Organizational and training issues in the Glendale Police and Fire Departments contributed to 11 Glendale police officers being exposed to chlorine.
- Published guidance on scrubber over-chlorination provided no specific information on the composition, quantity, or duration of emissions expected during over-chlorination incidents, delaying stabilization of the scrubber and extending the duration of the incident.

This CSB report makes recommendations to DPC Enterprises, the Glendale Fire and Police Departments, Maricopa County, and The Chlorine Institute.

1.0 Introduction

1.1 Background

At about 11:30 a.m. on November 17, 2003, an uncontrolled decomposition reaction in a batch scrubber released chlorine gas into the air at the DPC Enterprises, L.P. (DPC) chlorine repackaging facility in Glendale, Arizona. Hazardous emissions continued for about six hours. Residents and workers in a 1.5 square mile zone were told to evacuate, and 11 police officers and five members of the community sought medical treatment for exposure to chlorine.

Because of the serious nature of this incident, which followed a large scale chlorine release from a DPC facility in Festus, Missouri, in 2002,[1] the U.S. Chemical Safety and Hazard Investigation Board (CSB) launched an investigation to determine root and contributing causes, and to make recommendations to help prevent similar incidents. The Industrial Commission of Arizona (State OSHA program); U.S. Environmental Protection Agency (EPA); and the Maricopa County Environmental Services Air Quality Division also investigated.

1.2 Investigative Process

The CSB investigators arrived at the DPC Glendale facility one day after the incident. The CSB interviewed DPC employees and emergency responders, reviewed company documents, consulted scientific publications and experts, and examined physical evidence. The investigation focused on DPC's operating procedures and practices, its hazard assessment process, and its application of safeguards to prevent or mitigate reactive hazards. The CSB held a community meeting on June 9, 2004, in Glendale,

[1] DPC Enterprises had a chlorine release of 48,000 pounds at its Festus, Missouri, site on August 14, 2002. CSB Report No. 2002-04-I-MO, issued May 2003 and available at www.csb.gov, describes the CSB's findings and recommendations for the Festus incident.

Arizona, to update the community on the preliminary findings of the investigation and gather input from the emergency responders, community leaders, and the public.

1.3 Characteristics of Chlorine

1.3.1 Health Hazards of Chlorine

Chlorine, a powerful oxidizer, is so highly toxic that it was used as a poison gas in World War I. Chlorine attacks the lungs, causing inflammation (pneumonitis) and fluid accumulation (pulmonary edema), and is intensely irritating to the eyes; prolonged and/or acute exposure may be fatal. Table 1 summarizes typical symptoms of exposure to various concentrations of chlorine.[2]

Concentration (ppm in air)	**Health Effects**
1-3 ppm	Mild mucous membrane irritation
5-15 ppm	Upper respiratory tract irritation
30 ppm	Immediate chest pain, vomiting, shortness of breath (dsypnea) and cough
40-60 ppm	Inflammation of lung tissues (toxic pneumonitis) and fluid accumulation (pulmonary edema)
430 ppm	Death within 30 minutes
1,000 ppm	Death within a few minutes

Table 1. Health effects of acute chlorine exposure[3]

Because chlorine releases can produce effects toxic to humans, animals, and plants at considerable distances, identifying and controlling possible emission sources is extremely important.

[2] Government agencies, including the Occupational Safety and Health Administration (OSHA) and the National Institute for Occupational Safety and Health (NIOSH), and industrial hygiene associations, including the American Industrial Hygiene Association (AIHA), have established exposure limits for chlorine. Appendix A, Table 2A documents selected limits.

1.3.2 Physical Properties

Chlorine is a greenish-yellow gas 2.5 times heavier than air at normal pressure and temperature. Chlorine releases usually stay close to the ground and dissipate relatively slowly. See Appendix A for additional physical properties of chlorine.

1.3.3 Manufacture and Uses of Chlorine

Manufacturers produced 12.5 million tons of chlorine in the United States in 2002.[4] Chlorine is used to disinfect drinking water, and in the manufacture of bleach, paper, pesticides, solvents, medicines, and plastics, such as polyvinyl chloride (PVC).

Chlorine is shipped as a liquid under pressure at ambient temperature. Large users may receive chlorine in railcar (90 ton) quantities. Smaller users typically receive chlorine in 150-pound cylinders, 1-ton containers, or 17-ton bulk road trailers.

2.0 DPC Enterprises, L.P.

2.1 Corporate Structure

DPC Enterprises, L.P., is privately held and owns and operates six chlorine repackaging facilities. The company employs 50, including nine at the Glendale site. Publicly available sources and the company website indicate that DPC Enterprises is part of a family of companies, the DX Group[5] headquartered in Houston, Texas, with interests in organic chemicals manufacturing, oil well drilling additives, chemical distribution, and other businesses.

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[3] Ellenhorn and Barceloux, 1988.
[4] Source – The Chlorine Chemistry Council.
[5] From http://www.dxgroup.com

A centralized group in Houston provides management, engineering, health, safety, environmental, and security services to both DPC Enterprises and DPC Industries. Services include developing standard operating procedures (SOPs) and related training materials, and coordinating regulatory compliance activities, including those related to OSHA (Process Safety Management) and EPA (Risk Management Program) process safety regulations.

2.2 Glendale Site

Chlorine operations in Glendale, Arizona, were established by McKesson in 1965. Van Waters & Rogers (VWR) bought the facility in 1986. DPC Enterprises, L.P. acquired the site from VWR in 1999 and subsequently upgraded the facilities.

The surrounding community includes residential areas to the northeast and southwest, the Andalucia Elementary School, Maryvale Hospital, and a variety of retail businesses (Figure 1). Camelback Road and Grand Avenue are heavily traveled local roads. Glendale is a city of 234,000 (2003 estimate) on the west side of the Phoenix metropolitan area (Maricopa County).

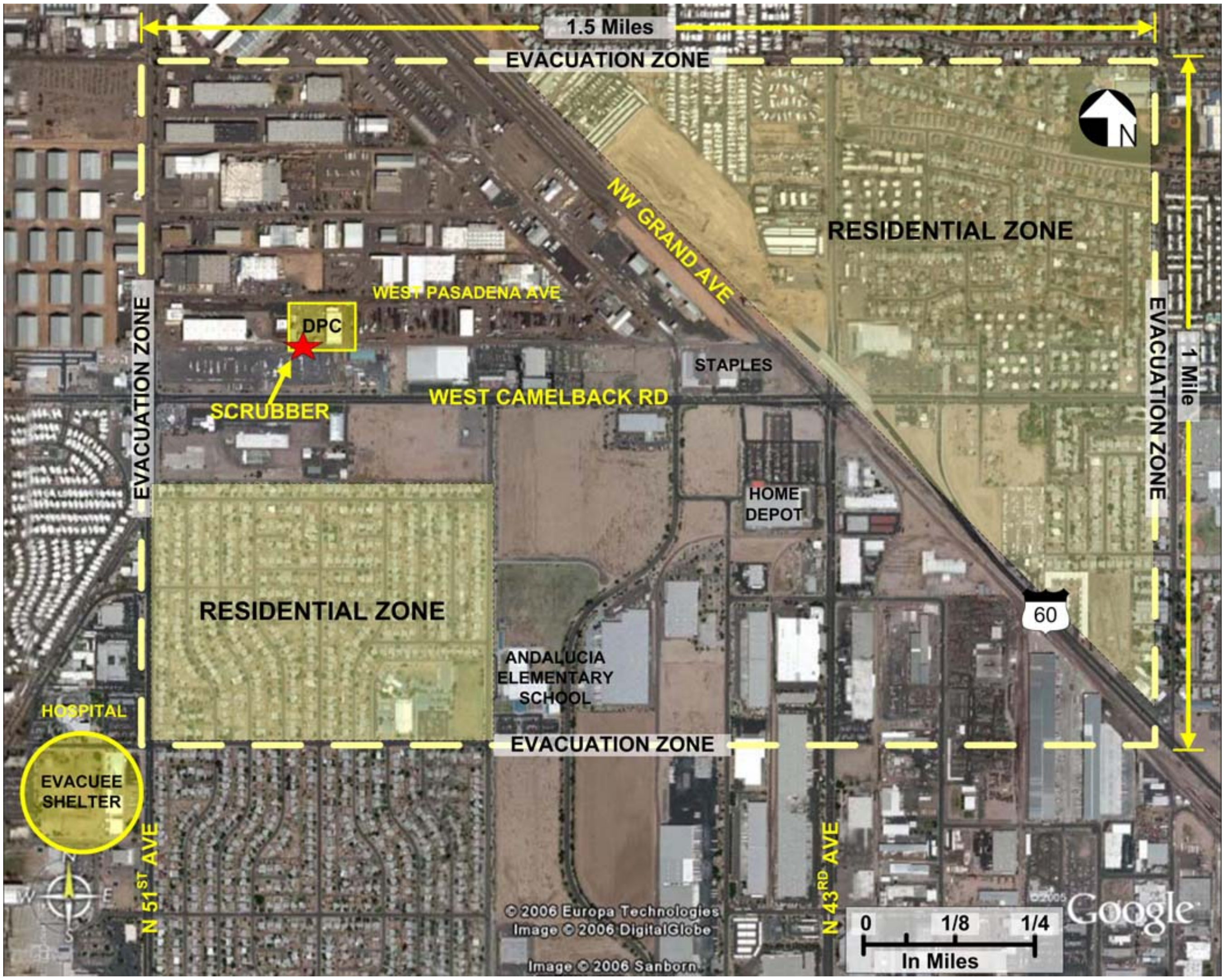

Figure 1. Surrounding community (Glendale and Phoenix, Arizona)

2.3 Process Description

At the site, DPC receives liquid chlorine in railcars and repackages it into smaller containers to distribute to local customers, and also manufactures sodium hypochlorite (or bleach). Figure 2 is a plot plan of the site, and shows the location of the major equipment involved in the November 17, 2003, incident. The caustic scrubbers used to control chlorine emissions are located in the southwest section, adjacent to the chlorine railcar unloading and bulk road trailer loading area. The chlorine building contains cylinder loading and bleach manufacturing facilities.

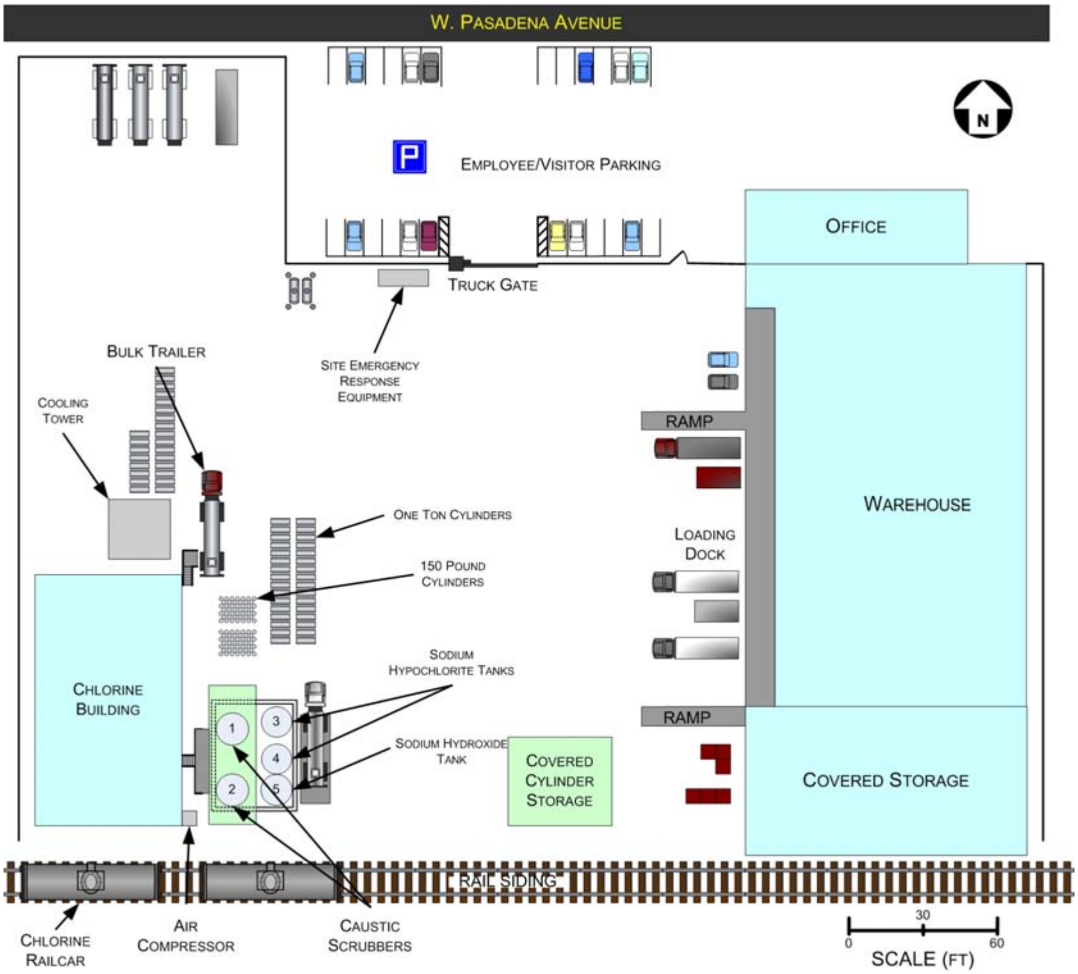

Figure 2. DPC-Glendale plot plan

2.3.1 Bulk Road Trailer Loading

About once a month, DPC supplies a bulk road trailer of chlorine to a local municipal water treatment facility. To transfer the chlorine, hoses specifically designed for chlorine service connect the chlorine railcar and the bulk road trailer (Figure 3 and Figure 4) to the transfer piping system. Remotely operated valves on each end of the hoses shut off chlorine flows in an emergency.[6] The railcar initially contains

[6] The chlorine release at the DPC Enterprises site in Festus, Missouri, resulted from the rupture of a transfer hose inadvertently fabricated using non-chlorine resistant materials, and the failure of remotely operated emergency valves to close. For a full discussion, visit the CSB website at www.csb.gov and download report 2002-04-I-MO.

liquid chlorine with a mixture of chlorine vapor and air in the headspace; the trailer usually contains air but little or no liquid chlorine.

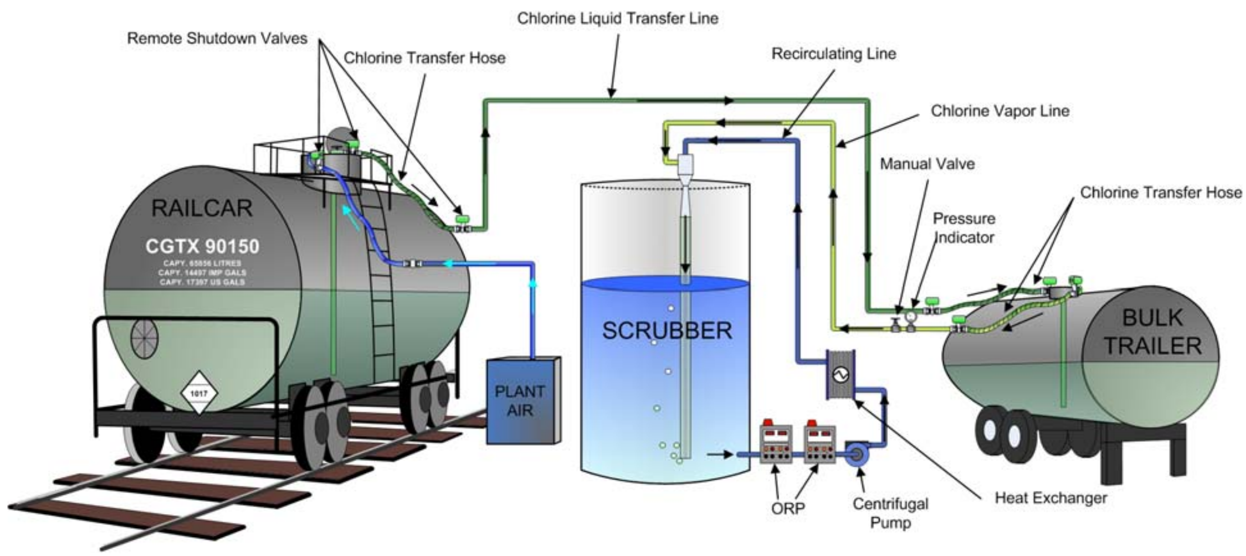

Figure 3. Chlorine bulk road trailer loading and caustic scrubber systems

Compressed air from the plant air supply pressurizes the headspace of the railcar and forces liquid chlorine to flow through the chlorine liquid transfer hoses and line into the bulk road trailer. As the bulk trailer fills, displaced chlorine vapors and air vent to one of two scrubbers.

Figure 4. Chlorine bulk road trailer

2.3.2 Scrubber Operation

The Glendale scrubbers have two purposes:

1. To capture (scrub) chlorine vented from repackaging operations (to protect workers and the public from exposure to chlorine).

2. To produce saleable bleach (sodium hypochlorite solution) for distribution to local industrial and commercial customers.

Because the optimum operating conditions for these two purposes are not identical,[7] operating the scrubbers simultaneously as critical safety devices and as batch bleach production units requires great care, and can greatly increase the risk of toxic releases.

Chemistry

Inside the scrubber, chlorine contacts a sodium hydroxide (caustic soda, NaOH) solution at a controlled temperature. The resulting reaction removes the chlorine and produces bleach (sodium hypochlorite, NaOCl); common salt (NaCl) is produced as a byproduct and remains with the bleach as a harmless impurity. Complete depletion of the caustic eliminates the scrubber's ability to capture chlorine. Moreover, depletion also initiates a rapid decomposition of the bleach, referred to in the bleach industry as "over-chlorination," which can release toxic chlorine compounds into the air (Appendix B).

Design and Control

The two Glendale scrubbers are 4,000 gallon, fiberglass reinforced plastic tanks (Figure 5).They operate as batch chemical reactors, with one unit receiving chlorine (the online scrubber), and the other operating as a backup (the standby scrubber).[8] Operators initially fill a scrubber with an aqueous solution containing 21 percent caustic.[9] Chlorine vented from repackaging operations is fed to the scrubber until the caustic concentration reaches 0.2-0.5 percent, as required by customer specifications for bleach.[10] The chlorine flow is then manually switched to the standby unit, the product bleach transferred to storage, and the depleted scrubber charged with fresh caustic solution.

[7] Scrubbing efficiency is best at caustic concentrations above 8 percent; commercial specifications for bleach require much lower caustic concentrations.

[8] The scrubbers are arranged in parallel–one unit cannot treat the gases vented from the other.

[9] The 21 percent caustic solution yields the desired concentration of product bleach.

[10] Chlorine can also be fed directly to the scrubbers to complete a batch or when demand for bleach is high.

As Figure 3 shows, a centrifugal pump circulates the scrubber solution through monitoring equipment and a heat exchanger (cooler) to the top of the scrubber where it mixes with chlorine vapors.[11] The cleaned air vents through the top of the scrubber. Scrubber efficiency is normally close to 100 percent.

Figure 5. Caustic scrubber (typical)

Two oxidation reduction potential (ORP)[12] meters located in the suction line to the pump (Figure 3) track the concentration of caustic in the scrubber liquid. The meter readings are displayed in millivolts (mV)

[11] The scrubbers use venturi contactors, which maintain a slight vacuum on the chlorine vent lines to reduce leaks to atmosphere.

[12] Oxidation-reduction potential measures a solution's ability to oxidize (accept electrons from) materials. Sodium hypochlorite is an oxidizer, and ORP measurements can be used to approximate the increase in bleach and corresponding decrease in caustic concentrations as the caustic reacts with chlorine.

on a local panel (Figure 5). The ORP meter readings increase as the residual caustic concentration in the scrubber solution decreases. The correlation between ORP readings and caustic concentration is normally highly repeatable, but can be affected by a variety of factors, such as temperature, fouling, and the initial caustic concentration (see section 4.1). Each ORP meter is equipped with two alarms to help operators track the depletion of caustic in the bleach batch (Table 2); however, no automated control actions occur based on the ORP meters' outputs.

	Alarm Setpoint Value (millivolts)	**DPC Operator Action Required**
First ORP Alarm (Process Meter)	500 mV (approx 1.5% excess caustic)	• Acknowledge alarm • Remain in area • Sample and perform laboratory analysis at 15-minute intervals
Second ORP Alarm (Process Meter)	515 mV (approx 1.35% excess caustic)	No action specified
Third ORP Alarm (Safety Meter)	530 mV (approx 1% excess caustic)	• Acknowledge alarm • If venting at a high rate: o Stop chlorine flow to scrubber o Sample and perform laboratory analysis at 5-minute intervals
Fourth ORP Alarm (Safety Meter)	545 mV (approx 0.66% excess caustic)	No action specified
		Stop scrubbing operations when excess caustic between 0.2–0.5% based on laboratory analysis

Table 2. Oxidation reduction potential (ORP) alarm setpoints and actions

A batch of bleach is complete when laboratory (off-line) analysis of the scrubber solution indicates that the residual caustic concentration meets DPC customer specifications of 0.2-0.5 percent.[13]

3.0 Incident Description

3.1 Incident

On November 17, 2003, DPC personnel were transferring chlorine from a railcar to a bulk road trailer when the scrubber became over-chlorinated and began releasing chlorine to the atmosphere.

At approximately 7:00 that morning, in preparation for the chlorine transfer, operators recorded the Oxidation Reduction Potential (ORP) meter reading of 490 mV and tested the solution in the scrubber. They measured a caustic concentration of 1.60 percent caustic (by weight), indicating that the scrubber had not yet reached its target concentration of 0.2-0.5 percent.

Shortly after 9:00 a.m., the operators began transferring chlorine to the bulk road trailer.[14] Air and chlorine vapors from the trailer flowed to the scrubber (Figure 3), reducing the caustic concentration. Operators continued working on other assigned tasks.[15] At 10:00 a.m., operators recorded an ORP reading of 510 mV, again tested the scrubber's contents, and recorded the caustic concentration at 1.18 percent.

According to the operators, the first safety alarm on the caustic scrubber, set at an ORP reading of 530 mV, activated at approximately 10:15 a.m. An operator pressed the acknowledge button to silence the alarm, checked the ORP value, and returned to other tasks.

[13] The caustic concentration in the scrubber solution is determined by laboratory analysis to evaluate the remaining capacity of the scrubber to react with chlorine vapors.

[14] The operators tested emergency shutdown systems and conducted leak checks before starting the chlorine transfer.

Shortly after 11:00 a.m., the second safety alarm, set at an ORP reading of 545 mV, activated. An operator pressed the alarm acknowledge button to silence the alarm and went to get a container for a scrubber solution sample. Upon returning to the scrubber area, the operator heard rumbling and saw liquid splashing from, and a green cloud forming around, the scrubber.

3.1.1 Emergency Shutdown/Facility Evacuation

The operator instructed nearby personnel to evacuate and pushed an emergency shutdown button,[16] which closed automatic valves on the loading line and the scrubber vent line connected to the bulk road trailer (Figure 3). He activated the plant's emergency alarm, and evacuated with other DPC employees to the designated assembly area. DPC's plant manager called 911 and then telephoned neighboring businesses to inform them of the release.

3.1.2 Emergency Response

The Phoenix Fire Department was first to arrive on the scene, and were joined by the Glendale and Tempe fire departments and the Glendale and Phoenix police departments.

Responders established initial boundaries for the potentially hazardous area, and later expanded the boundaries when plume modeling by the Tempe Fire Department indicated that the potentially hazardous area could be larger.

Authorities used an automated telephone call-down system and media announcements to notify the community in the potentially hazardous area to evacuate. Police officers also drove through the evacuation area and used their public address systems to notify residents. None of the officers who entered the potentially hazardous area wore respiratory protection. The evacuated area included about

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[15] One operator filled drums of bleach, while another transferred 50-weight percent caustic solution from a railcar to a storage tank, and moved bleach drums to storage.

[16] Testing conducted by the CSB after the incident verified that the emergency shutdown system operated properly.

2,500 homes with 7,200 residents, and several large businesses (Figure 1). Students at the Andalucia Elementary School sheltered-in-place.[17]

Responders set up water sprays to absorb chlorine gas, and entered the site at approximately 1:30 p.m. to close manual valves associated with the railcar, bulk road trailer, and scrubber. Phoenix Fire Department responders measured chlorine concentrations of 20-35 parts per million (ppm) close to the scrubber, with higher spikes when gases periodically vented. The rate of venting eventually decreased, and all evacuees were allowed to return to their homes about four and one half hours after the over-chlorination of the scrubber.

Minor venting of chlorine from the scrubber continued until DPC personnel added caustic to the scrubber to stabilize the contents and absorb any remaining chlorine. No further emissions were detected.

As a result of the incident, 11 police officers and five citizens were evaluated for symptoms consistent with chlorine exposure.

4.0 Incident Analysis

4.1 Operating Practice versus Procedure

Bleach manufacturing practice[18] at the DPC Glendale site deviated significantly from the written SOPs when chlorine vented to the scrubber at a high rate.

DPC's written bleach production SOPs required that the chlorine flow to the scrubber be shut off and that the scrubber solution be sampled at five-minute intervals when the Oxidation Reduction Potential (ORP)

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[17] To shelter-in-place is to remain indoors while restricting the ability of toxic substances to enter by turning off ventilating systems, moving to interior rooms, and sealing openings.

[18] Practice is how operators actually perform a task. Procedure is how the SOP specifies performing that task.

meter reading reached 530 mV and chlorine was venting to the scrubber at a high rate. DPC management considered bulk road trailer loading to produce a high rate of venting.

In practice, however, operators continued the flow of chlorine to the scrubber until the target concentration was reached, while periodically sampling the scrubber solution. On the day of the incident, the scrubber over-chlorinated while the operator was preparing to take a sample for laboratory analysis.

Several characteristics of the DPC process made the scrubber susceptible to over-chlorination:

- At the target concentration of 0.2-0.5 percent caustic, only 1-2 percent of the initial caustic charge remained, leaving little reserve to protect the scrubber in case of changes in chlorine flow rate or delays in operator response near the end of a batch.

- Chlorine flow to the scrubber varied greatly. Based on production log entries, CSB investigators calculated that the flow of chlorine gas from the bulk road trailer to the scrubber at least tripled toward the end of the transfer on the day of the incident.[19]

- The ORP meter readings were susceptible to errors due to a variety of factors, including temperature swings, changes in the initial caustic concentration, variation in the chemistry of the water used to prepare the caustic solution, sensor fouling, and installation-specific factors. These potential error sources would similarly affect both ORP probes.

These factors combined to make the time between sounding of the final ORP alarm and over-chlorination both variable and difficult to predict. Together with the operating practice of maintaining chlorine flow to the scrubber while sampling, this greatly increased the risk of scrubber over-chlorination.

[19] The flow of chlorine likely tripled because the gas initially vented from the trailer contained appreciable amounts of nitrogen. As the trailer filled with liquid, the vented gas became chlorine enriched.

In addition, DPC management failed to recognize that practice deviated from the written bleach production SOP.

4.2 Scrubber Operating Procedure and Training

The bleach production (scrubber) SOP did not reflect the sensitivity of the process to over-chlorination. Furthermore, it did not provide operators with key information about the consequences of deviating from operating limits:

- The SOP warned that relying on the ORP meters to determine excess caustic could result in over-chlorination with the "possible" release of chlorine, and directed operators to verify ORP readings using laboratory measurements. However, it did not indicate clearly why or how the ORP readings could vary or that an incident with potentially serious off-site safety and environmental consequences could result.

- The SOP specified no actions to be taken upon receipt of the fourth (final) alarm (such as double-checking that the chlorine flow was shut off before sampling), and contained no warning that the time between this alarm and over-chlorination could be brief.

- The SOP did not document which operations produced high rates of chlorine venting, and thus required more conservative operation of the scrubber. As a result, the operators were unaware that bulk road trailer loading was considered to be a high vent rate operation.

- The SOP was available for employee review, but was not routinely used in daily operation. The operators stated that they were unfamiliar with all the requirements of the SOPs.

Operator training, based on the operating procedure, did not address the sensitivity of the scrubber to over-chlorination or the safety and environmental consequences of over-chlorination.

Operators are far more likely to follow procedures when they understand why and under what circumstances specific actions are required (CCPS, 1994, 1996). Operating procedures for hazardous processes thus need to provide clear guidance on the consequences of deviation and the steps needed to correct or avoid such deviations [§OSHA 1910.119(f)(ii)], and on any special circumstances that require changes to normal practice. Managers also need to monitor actual practice to ensure that procedures are followed.

4.3 Hazard Assessment and Control

The November 17 chlorine release was serious, and had the potential to significantly harm workers and the community. The CSB investigators estimate that the scrubber could have released up to 1,920 pounds of chlorine (Appendix B). Fortunately, the weather conditions during the incident were favorable for dissipation of the release. Under these conditions, the CSB estimates that hazardous concentrations[20] of chlorine likely extended out as far as 0.4 miles from the site.[21] A similar release under highly stable atmospheric conditions could produce toxic concentrations of chlorine up to 1.3 miles from the DPC site.

The areas of Glendale and Phoenix within these distances of DPC are shown in Figure 6. Approximately 750 people live inside the smaller (0.4 mile radius) circle (Region 1), while nearly 30,000 live inside the larger (1.3 mile radius) area (Region 2). Depending on the wind direction and atmospheric conditions, a 1,920 pound release in this densely populated area could place many people at risk.

[20] Based on reaching chlorine's Emergency Response Planning Guideline (ERPG)-2 concentration of 3 ppm at the distances given. Concentrations closer to the DPC site would have been higher. The ERPG-2 concentration is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing irreversible or other serious health effects, or symptoms that could impair an individual's ability to take protective action (American Industrial Hygiene Association). The EPA and other organizations use ERPG-2 concentrations in emergency response planning. Exposure to lower concentrations of chlorine can still cause symptoms, see Table 1.

[21] The release occurred during the day and with moderate winds, conditions that favored rapid dispersion of the release. Highly stable atmospheric conditions, such as often occur at night, could slow dispersion and increase the toxic endpoint distance.

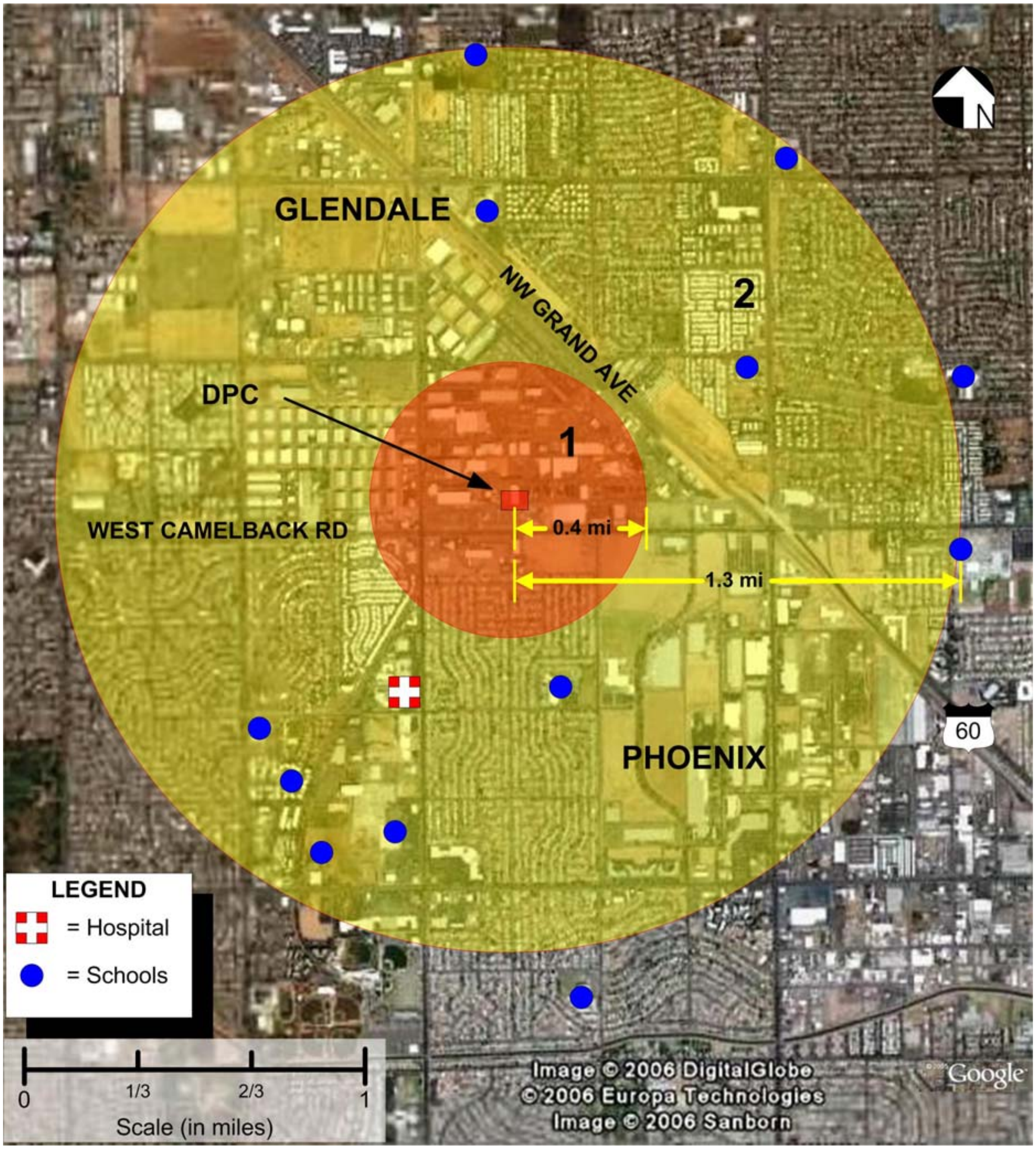

Figure 6. Hazardous chlorine concentration distances

4.3.1 Matching Safeguards to Risk

DPC relied on a single administrative safeguard to prevent scrubber over-chlorination: an SOP. While SOPs are essential in any process safety program, such procedures are regarded as the least reliable form of safeguard in preventing process incidents. The Center for Chemical Process Safety (CCPS) (2004) has ranked safeguards in decreasing order of reliability:

Reliability	Type	Examples
Most Reliable	Passive Safeguards	• Reduced inventory of hazardous substances • Use of chemistry with reduced toxicity
Less Reliable	Active Safeguards	• Emergency shutdown systems • Downstream (secondary) scrubbers
Least Reliable	Procedural Safeguards	• Operating procedures

Table 3. Safeguard reliability[22]

Passive safeguards, such as reduced inventory of hazardous substances, cannot readily fail, but, as in this case, are not always feasible. Active safeguards, such as emergency shutdown systems, must be maintained and tested, and may suffer from shared (common mode) failure mechanisms such as the loss of utilities, making them potentially less reliable than passive safeguards. Procedural safeguards, such as SOPs, rely on personnel consistently making correct and timely decisions while performing other duties, and potentially while stressed or fatigued. Procedural safeguards are thus considered to be the least reliable of the three types.

Failures with potentially severe consequences, such as a chlorine release in a densely populated area like Glendale, may require multiple, independent safeguards, in addition to procedures that, in aggregate, have the effectiveness and reliability needed to prevent, control, or mitigate the consequences of critical failures.

[22] CCPS, 2004.

Examples of active safeguards that could reduce the likelihood or reduce the consequences of scrubber over-chlorination include (but are not limited to):

- Automatic shutoff of the chlorine upon high ORP alarm to prevent over-chlorination.[23]
- A downstream scrubber to treat the gases released by over-chlorination. The standby scrubber could be configured for this or a dedicated emergency scrubber installed.
- Automatic or remote injection of caustic into an over-chlorinated scrubber, which could stabilize the scrubber quickly and prevent the extended release of toxic materials.[24]

Additional procedural safeguards, such as stopping the chlorine feed to the scrubber at a higher caustic concentration and completing the bleach batch in Glendale's continuous bleach manufacturing system, could also reduce the likelihood of over-chlorination, but should be combined with active safeguards to reliably protect against the consequences of over-chlorination.

In addition, methods such as Layers of Protection Analysis (LOPA) have been developed that can help companies assess if their safeguards will effectively and reliably control serious hazards (CCPS, 2001). Chlorine scrubbers, which are batch reactive systems with high-consequence failure modes, are good candidates for evaluation using LOPA.

4.3.2 Process Hazards Analysis

Hazards at chemical facilities are usually identified, and their potential for causing harm estimated, in a Process Hazard Analysis (PHA). DPC performed a PHA of the Glendale chlorine system in 1999 when

[23] Stopping chlorine flow to the scrubber after over-chlorination has begun will not stop the bleach decomposition reaction, although it will reduce the emission of unscrubbed chlorine.

[24] All these measures are used at other bleach manufacturing facilities in the US, according to a survey by The Chlorine Institute, and may be considered best practices.

DPC had just acquired the site, and another in 2001 when the company installed a continuous bleach production process. While the PHAs evaluated a variety of equipment failure mechanisms, they did not review the scrubber operating procedure and did not directly address failure to turn off the chlorine flow to the scrubber at the end of a batch.[25]

DPC estimated that the scrubber released 3,500 pounds of chlorine during the November 17, 2003, incident, a quantity that could cause serious off-site consequences (see section 4.3).[26] DPC could and should have made this estimate as part of its risk assessment process before the incident and taken steps to reduce the likelihood or severity of scrubber over-chlorination.

While the "What If?" checklist PHA method DPC used for both studies is a recognized approach, relying on checklists can impede the identification of unusual or not previously recognized hazards. Good practice is to use a variety of methods when revalidating PHAs for highly hazardous processes, as using different PHA methods will, over time, provide a more complete assessment of hazards.

The Glendale PHAs did not identify and address the known scrubber failure mode of over-chlorination. Companies should review their chlorine scrubber PHAs to ensure that scenarios potentially leading to over-chlorination have been identified and reviewed, and that adequate safeguards are in place to control this serious hazard. Guidance for planning and conducting effective PHAs is provided in many CCPS publications (1995, 1999, 2001).

[25] DPC is required by OSHA Process Safety Management and EPA Risk Management Program regulations to perform or revalidate PHAs at specified intervals and after significantly changing the chlorine handling processes at the facility.

[26] DPC based its estimate of 3,500 pounds on the release of most of the chlorine fed to the scrubber. The CSB estimate of up to 1,920 pounds is an upper limit based on the chemistry described in Appendix B.

4.3.3 Process Safety Management Audits

The Glendale site is covered by OHSA's Process Safety Management (PSM) regulation (see section 4.6.1). 29 CFR 1910.119 (o), "Compliance Audits" requires employers to "certify that they have evaluated compliance with the provisions [of the regulation] at least every three years to verify that the procedures and practices developed under the standard are adequate and are being followed." These audits provide critical feedback and correction to maintain PSM program effectiveness.

A manager from DPC's corporate health, safety, environmental, and security group performed a PSM-required audit of the Glendale facility in June 2002. The checklist-based one-day audit generated only eight recommended actions, including six that addressed documentation, and found that all procedures, training, and process safety information were up-to-date and accurate.

This audit failed to detect the missing process safety information and scrubber operating procedure problems uncovered during the CSB's investigation. For example, no Piping and Instrumentation Diagrams (P&IDs) existed for the site prior to the November 17, 2003, incident, although the PSM regulation specifically requires them.

The audit did not rigorously examine the underlying PSM program elements; rather, the focus was on whether the PSM program procedures developed by the corporate support group were in place at the site. Moreover, the same corporate group performing the audit had also developed the site PSM program, written the site operating procedures, and participated in or led the site PHAs. The weaknesses in PSM program elements the CSB identified in its investigation are not readily detectable using such an audit approach.

Companies can benefit by incorporating independent auditors into their safety program. Using multi-person audit teams can also lead to higher quality audits by providing a variety of insights into program elements and their implementation. The CCPS (1993) publishes guidelines that can help companies plan and perform effective audits.

4.3.4 Voluntary Safety Management Systems

Voluntary safety management systems (vSMS) can provide access to state-of-the-art management practices, expert advice, a common framework for all sites, guidance on continuous safety improvement, and objective feedback on safety system implementation. Table 4 lists several notable examples of such programs.

DPC Enterprises' sites have not yet been verified and certified under a voluntary safety system. Their safety performance could benefit from such verification and certification.

Program	**Sponsoring Organization (web page)**
Responsible Distribution™	National Association of Chemical Distributors (www.nacd.com)
Responsible Care™	American Chemistry Council (www.responsiblecare.com)
Voluntary Protection Program	OSHA (www.osha.gov/dcsp/vpp)

Table 4. Voluntary safety management systems

4.4 Emergency Management

4.4.1 DPC Emergency Planning and Response

Prior to the incident, DPC Glendale provided local emergency responders with information on hazardous chemicals at its facility and on the company emergency response plan, as required by EPA's Emergency Planning and Community Right-to-Know Act (EPCRA) and RMP regulations.

Company personnel followed DPC's emergency response plan during the incident. The operator activated the emergency shutdown system, shutting off the chlorine flow to the bulk road trailer and the scrubber.[27] He also activated the plant alarm system, after which DPC personnel evacuated the facility without mishap. The plant manager notified emergency responders and adjacent facilities of the release.

In addition, plant management personnel remained on the scene. They provided responders with an estimated release quantity of 3,500 pounds of chlorine, and with information on valve locations to help firefighters ensure that the scrubber was isolated from all chlorine sources.

4.4.2 Public Agency Emergency Response

The responding fire departments rapidly activated a unified command structure, and established an incident command center near the DPC site.[28,29] The Glendale, Phoenix, and Tempe fire departments contributed resources to the response. Fire department communications worked well throughout the incident. County and state agencies also responded and provided environmental monitoring and other assistance.

The incident commander established an initial isolation zone covering roughly two city blocks, based on the *DOT Emergency Response Guidebook's* recommendations for chlorine releases, and excluded traffic from a segment of Camelback Road (a major east-west roadway). Based on dispersion modeling by the Tempe Fire Department,[30] the incident commander expanded the isolation zone to a 1 by 1.5 mile rectangle extending downwind from the DPC site (Figure 1).

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[27] Post-incident testing witnessed by the CSB confirmed that the isolation valves operated properly and did not leak. Chlorine flow to the scrubber likely stopped within 1-2 minutes of the start of the incident.

[28] The responders followed a standard protocol for emergency response based on the National Incident Management System (NIMS), established through the Department of Homeland Security. See www.dhs.gov/dhspublic/interapp/press_release/press_release_0363.xml .

[29] Phoenix area fire departments share a common dispatch system and routinely provide emergency services across city lines. These departments also participate in a regional response plan through the Maricopa County Department of Emergency Services or the Arizona Division of Emergency Management.

[30] Tempe personnel were equipped with and trained on the use of the EPA CAMEO (Computer Aided Management of Emergency Operations) software. They used the ALOHA (Areal Locations of Hazardous Atmospheres) dispersion modeling program, included with CAMEO, to estimate the potential extent of the toxic cloud.

The incident commander, in consultation with fire department personnel,[31] ordered the evacuation of most of the isolation zone and sheltering-in-place for students at the Andalucia Elementary School. City buses were used to transport residents to a refuge location southwest (upwind) of the evacuation zone, south of the Maryvale Hospital (Figure 1).

Glendale and Phoenix police controlled access to the isolation zone and notified residents of the evacuation order using their squad car public address systems. The Glendale City and Maricopa County telephone call-down systems and the local media were also used to contact residents and inform them of the need to evacuate.[32]

Emergency responders suspected that chlorine might be leaking from the chlorine railcar because of the extended duration of the chlorine emissions. They closed manual valves on the railcar and bulk road trailer; however, emissions continued, albeit at a decreasing rate, until DPC personnel added caustic to the scrubber, stabilizing it.

Air quality monitoring by the Arizona Department of Environmental Quality (ADEQ) continued until the scrubber was secured and all emissions had ceased. The incident commander closed the incident at 8:54 p.m.

The size of the release, the favorable weather conditions, and the emergency response efforts in this incident limited the community's exposure to chlorine. Five residents exposed to low concentrations of chlorine were transported for medical evaluation, examined, and released.

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[31] Shelter-in-place decisions can be complex, and involve balancing the potential hazard of remaining at the shelter location with being exposed to toxic material while attempting to evacuate.

[32] Technical and coordination issues with the call-down systems caused some confusion. Glendale residents received messages from both the City and County systems. The County system's message began clearly in Spanish, but the volume then dropped, making the English portion of the message unintelligible. This led to the Glendale 911 center being inundated with calls. The Glendale system has since been shut down and replaced by the Maricopa County system.

4.4.2.1 Police Chlorine Exposure

The Glendale Police Department provides its officers with air purifying respirators (APRs) designed to protect them from the effects of toxic gases. The 11 Glendale Police Department officers[33] treated for chlorine exposure were not wearing their APRs when they were exposed because:

- The incident command system did not deliver timely information about the location of chlorine-contaminated areas to the officers. This was due to poor integration of the police into the incident command structure and technical factors, including incompatible fire and police radio frequencies. Officers were not always aware they were entering a contaminated area.

- Police dispatchers sent officers directly into the isolation zone without first directing them to a staging area where they could be briefed on incident conditions, review Glendale Police Department safety procedures for hazardous materials incidents, and check their personal protective equipment (PPE). As a result, some officers did not have their APRs with them.

- Some officers carrying APRs failed to use them. They interpreted warnings from fire department personnel to mean that the police APRs offered no protection against chlorine, when, in fact, their APRs would have been highly effective.[34]

Failure to use PPE reflects a need for training beyond the officers' First Responder–Awareness level. Officers' duties during this incident included evacuating citizens from potentially chemically affected areas, making First Responder - Operations level training more appropriate.[35] The exposed officers had

[33] Nine officers were taken to hospitals, evaluated, and released; two were evaluated at the scene and released.

[34] APRs are not permitted when hazardous materials are above the "Immediately Dangerous to Life or Health" (IDLH) concentration, which is 10 parts per million (ppm) for chlorine. Fire department responders were equipped with Self Contained Breathing Apparatus (SCBA), which are protective above the IDLH. Chlorine concentrations were above the IDLH close to the scrubber where fire department, but not where police, personnel were stationed.

[35] Training requirements are specified in OSHA 29 CFR 1910.120(q).

also not received their annual hazardous materials refresher training. Improved training would likely have increased APR use and reduced officer exposure to chlorine.

An earlier release at the site in 1988 also exposed Glendale Police Department officers to chlorine. Police must be integrated into the incident command structure, given timely hazard information, briefed on the hazards they face, checked to ensure they are carrying their PPE, and trained to recognize and effectively respond to hazardous materials incidents. Periodic hazardous materials exercises are also essential to ensuring that the Glendale Fire Department's and Glendale Police Department's response to future hazardous materials incidents protects the well-being of both the public and responders.[36]

4.5 Industry Guidance on Bleach Over-Chlorination

Scrubber over-chlorination is a documented hazard known to result in the release of toxic materials. To better understand the characteristics of scrubber over-chlorination, the CSB conducted an extensive technical literature search; reviewed guidance documents published by The Chlorine Institute (CI); and interviewed academic and industry experts. These sources generally agreed on the chemistry involved (Appendix B), but did not provide quantitative guidance on important features of over-chlorination incidents, such as:

- The total amount of toxic gases emitted during a release due to bleach decomposition.
- The identity of the major toxic materials released. While the assumption has been that it is chlorine, materials with different properties, such as hypochlorous acid, might also be released.
- The duration of the release.

[36] Resources for planning, executing, and evaluating hazardous materials exercises include the National Response Team's NRT-2 (1990) and the Department of Homeland Security's Homeland Security Exercise and Evaluation Program (2006).

- The impact of variation in scrubber operating conditions on release characteristics.
- Methods to control or mitigate over-chlorination events.

This information is needed to accurately design mitigation equipment, such as downstream (secondary) scrubbers, and to provide better guidance to emergency responders. In this incident, better information about the characteristics of over-chlorination incidents would likely have led to an earlier decision to add caustic to the scrubber, reducing the duration and impact of the incident.

The Chlorine Institute publishes guidance documents relevant to the design and operation of chlorine scrubbers used for bleach production,[37] including "Chlorine Scrubbing Systems, Chlorine Institute Pamphlet 89" and "Sodium Hypochlorite Manual, Chlorine Institute Pamphlet 96." These documents advise that over-chlorinating scrubbers is dangerous and can lead to the release of hazardous materials, including chlorine. However, the versions available at the time of the incident did not recommend specific safeguards to prevent, control, or mitigate the consequences of scrubber over-chlorination. The 2006 edition of Pamphlet 89 provides useful recommendations for scrubber safeguards, but not all of these would be effective in preventing or stopping bleach decomposition due to over-chlorination.

Public safety would benefit from additional guidance quantifying the consequences of scrubber over-chlorination and providing more comprehensive recommendations for best practices to prevent these dangerous events.

4.6 Regulatory Background

The OSHA PSM and the EPA RMP regulations are both intended to reduce the risk of catastrophic releases of highly hazardous chemicals. PSM focuses on how releases impact workers, while RMP

[37] DPC's corporate engineering and safety staff indicated that they refer to The Chlorine Institute's publications for guidance.

incorporates the elements of PSM and adds requirements for evaluating off-site consequences and community outreach. Because the Glendale site contains greater-than-threshold quantities of chlorine under both PSM (1,500 pounds) and RMP (2,500 pounds), DPC has compliance programs for both programs. The caustic scrubber is also permitted by Maricopa County as an air pollution control device.

4.6.1 The OSHA PSM Regulation

The CSB's investigation revealed significant weaknesses in the DPC Glendale PSM program, as discussed in Process Hazard Analysis-1910.119 (e) (Section 4.3.2); Operating Procedures–1910.119 (f) (Section 4.2); and Training–1910.119 (g) (Section 4.2).

4.6.2 The EPA RMP Regulation

The RMP regulation requires facilities to submit information on the potential off-site consequences of their operations, including the distance at which toxic effects could occur in the most probable serious accident at the site. This distance, the alternative case toxic endpoint distance, was reported by DPC as 0.6 miles for the Glendale site, close to the CSB-estimated distance for this incident.[38]

Based on the U.S. Census Bureau's Landview 6 mapping software, approximately 3,300 people live within DPC's alternative case distance. Thus, the most likely anticipated release scenario at the DPC facility would be expected to impact a large number of local residents. Approximately 7,200 live within the much larger area evacuated during this incident.

[38] The EPA also requires sites to report the worst case distance; in this case the complete discharge of a chlorine rail car in 10 minutes, under stable atmospheric conditions unfavorable for dispersion. For the Glendale site, this distance is 14 miles. Approximately 1.7 million people live within this radius of the DPC Glendale site.

4.6.3 Maricopa County Environmental Quality Division, Air Quality Department

Under an EPA State Implementation Plan (SIP), Maricopa County administers the pollution control permit program in Glendale. The County permitted DPC as a non-major source of chlorine emissions.[39,40] The permit required DPC to ensure that fill lines and hoses were vented “through a properly working scrubber that is maintained and operated in accordance with the approved operations and maintenance plan,” and to have and follow operating procedures to “minimize emissions from the transferring, handling, or repackaging” of chlorine.

The operations and maintenance plan submitted by DPC and approved by the County specified daily logging of ORP meter readings from the scrubber, but not of the more reliable laboratory measurements of caustic concentration.

[39] Non-major sources emit less than 10 tons per year of any single Hazardous Air Pollutant (HAP) and less than 25 tons per year of total HAPs. Chlorine was the only HAP permitted at the DPC Glendale site.

[40] No National Emissions Standard for Hazardous Air Pollutants (NESHAP) exists for chlorine. The EPA has determined that chlorine is not a persistent pollutant, in that it photolyzes rapidly to hydrochloric acid (HCl), a much less toxic substance, following release. The pollution control permit program is not designed to address major releases of highly hazardous materials, such as the November 17, 2003, DPC release.

5.0 Root and Contributing Causes

5.1 Root Cause

The safeguards provided on the DPC scrubber were not commensurate with the risk of over-chlorination.

- DPC's corporate standards relied solely on procedural safeguards against scrubber over-chlorination.
- DPC's corporate hazard assessment process did not identify or address the consequences of failure to follow the bleach manufacturing SOP, including potential off-site consequences.
- DPC's internal PSM/RMP audit program did not detect deficiencies in operating procedures, training, operating practice, process safety information, and hazard assessment.

5.2 Contributing Causes

1. Practice at DPC's Glendale site deviated from the scrubber SOP when chlorine was venting at a high rate, increasing the risk of scrubber over-chlorination.

- DPC's corporate scrubber SOP and training materials did not address the consequences of deviating from the scrubber SOP.
- Compliance with the scrubber procedure was not enforced, further weakening an already inadequate safeguard.
- Operators were inadequately trained on the consequences of over-chlorination and on the sensitivity of the process to over-chlorination.

2. Organizational and training problems contributed to the exposure of 11 Glendale Police Department officers to chlorine.

    - Inadequate integration of the Glendale Police Department into the incident command structure prevented the timely transmission of critical safety information to responding officers.

    - Deployment of Glendale Police Department officers into chlorine-impacted area without briefing or safety equipment checks allowed them to enter hazardous locations without APRs.

    - Inadequate hazardous material training led to Glendale Police Department officers not wearing their APRs.

3. Published guidance on scrubber over-chlorination does not provide specific information on the composition, quantity, or duration of emissions expected during over-chlorination incidents.

6.0 Recommendations

DPC Enterprises

1. Establish and implement DPC corporate engineering standards that include adequate layers of protection on chlorine scrubbers at DPC facilities, including

    - additional interlocks and shutdowns, such as automatically stopping chlorine flow to the scrubber upon oxidation-reduction potential alarm;
    - mitigation measures, such as systems to automatically add caustic to over-chlorinated scrubbers, or back-up scrubbing capability to treat emissions from over-chlorinated scrubbers;
    - increases in the final caustic concentration in the scrubbers to eight percent or higher to provide a substantial safety margin against over-chlorination; and
    - use of the site's continuous bleach manufacturing system to convert scrubber solution to saleable bleach.

2. Revise scrubber SOPs to include:

    - clearly described operating limits and warnings about the consequences of exceeding those limits, and
    - the safety and environmental hazards associated with scrubber over-chlorination.

3. Train employees on the revised SOPs and include a test to verify understanding. Periodically review operator understanding of and conformance to the scrubber SOPs.

4. Include scrubber operation in facility PHAs. Ensure that they:

   - include lessons learned from this incident and other DPC scrubber incidents, as well as industry experience with over-chlorination, and
   - consider off-site consequences when evaluating the adequacy of existing safeguards.

5. Use a qualified, independent auditor to evaluate DPC's PSM and RMP programs against best practices. Implement audit recommendations in a timely manner at all DPC chlorine repackaging sites.

6. Implement a recognized safety management system, including third party verification and certification, to achieve documented continuous improvement in safety performance at Glendale and the other DPC chlorine repackaging sites.

Glendale Fire Department

1. Work with the Glendale Police Department to integrate them into the incident command structure during hazardous material incidents, and address communications issues, such as radio interoperability, to ensure the timely transmission of critical safety information to responding officers.

2. Conduct hazardous materials exercises with the Glendale Police Department to identify and resolve police/fire integration issues. Coordinate exercise planning with the Arizona Division of Emergency Management Exercise Officer and with the Maricopa County LEPC. Schedule periodic hazardous materials incident drills to ensure safe and effective responses to future hazardous materials incidents.

Glendale Police Department

1. Work with the Glendale Fire Department to integrate the Glendale Police Department into the command structure during hazardous material incidents, and address communications issues, such as radio interoperability, to ensure the timely transmission of critical safety information to responding officers.

2. Ensure that police officers responding to hazardous material incidents are briefed on specific incident conditions, and are equipped with and trained on the proper use, capabilities, and limitations of appropriate protective equipment.

3. Ensure that police officers receive hazardous materials – operations level training, and annual hazardous materials and air purifying respirator (APR) refresher training.

4. Conduct exercises with the Glendale Fire Department to identify and resolve police/fire integration issues. Coordinate exercise planning with the Arizona Division of Emergency Management Exercise Officer and with the Maricopa County LEPC. Schedule periodic hazardous materials incident drills to ensure safe and effective responses to future hazardous materials incidents.

Maricopa County Department of Air Quality

1. Revise DPC's permitted operating conditions to specify a minimum scrubber caustic concentration of 8 percent or more, as determined by laboratory measurement, with measurements taken daily and upon completion of each scrubber batch.

The Chlorine Institute

1. Clarify the chemistry involved in over-chlorination incidents so that "Chlorine Scrubbing Systems, Pamphlet 89," and other pertinent publications:

    - Ensure that the recommended practices and safeguards prevent, mitigate, and control hazardous releases due to bleach decomposition.

    - Provide sufficient detail on the safety and environmental consequences of over-chlorination to enable companies to provide emergency responders with information on the potential characteristics of over-chlorination events, and on the best means of mitigating the bleach decomposition reaction following a release.

By the

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Appendix A Chlorine Physical Properties and Exposure Limits

Table 1A summarizes important physical properties of chlorine.

	Property	Value / Units
1	Molecular Weight[1]	70.9
2	Vapor Specific Gravity (Air = 1.0)[1]	2.45
3	Normal Boiling Point Temperature[1]	-29.2°F (-34°C)
4	Vapor Pressure at 32°F (0°C)[2]	38.9 psig
5	Vapor Pressure at 77°F (25°C)[2]	98.5 psig
6	Water solubility at atmospheric pressure and 77°F (25°C)[3]	6.4 grams/liter (slightly soluble)
7	Odor	Pungent / Penetrating[3]

Table 1A. Physical properties of chlorine

Sources:

1. CRC Press, 1980. *Handbook of Chemistry and Physics*, 61st ed, p. B-93.
2. AIChE, 2006. *Design Institute for Physical Properties, Project #801*, correlation for chlorine vapor pressure
3. The Chlorine Institute, 1997. *The Chlorine Manual*, Pamphlet 1, Edition 6, January 1997, p. 48.

Table 2A summarizes exposure limits for chlorine.

Standard Setting Body	Permissible Exposure, ppm	Description
NIOSH	0.5	Recommended Exposure Limit (REL)
OSHA	1.0	Permissible Exposure Limit (PEL)
NIOSH	1.0	Short Term Exposure Limit (STEL)
AIHA	3	Emergency Response Planning Guideline Level 2
NIOSH	10	Immediately Dangerous to Life or Health (IDLH)

Table 2A. Exposure limits for chlorine

The PEL (OSHA) and REL (NIOSH) are time-weighted exposure levels for routine worker exposure. The STEL (NIOSH) and the PEL are ceiling (maximum) exposure limits.

The Emergency Response Planning Guideline (ERPG) level 2 concentration is used to determine the toxic endpoint distance for estimating off-site consequences in the EPA's RMP program. EPRG concentrations are issued by the American Industrial Hygiene Association (AIHA).

Exposure to chlorine at concentrations at or above the IDLH (NIOSH) may make escape from a vapor cloud difficult due to severe eye and respiratory irritation. Serious health effects, including permanent harm, may also occur. Air purifying respirators (APRs), the type of respiratory PPE issued to the Glendale Police Department, may not be used in atmospheres containing chlorine concentrations above the IDLH.[1]

[1] APRs use absorbent cartridges to remove contaminants from breathing air. Saturation of the absorbent cartridges or leakage into the respirator's face mask may expose personnel to toxic concentrations of contaminants.

Appendix B Bleach Over-chlorination Chemistry

Based on an extensive literature search and discussions with industry and academic experts, the CSB has determined that the bleach in the DPC–Glendale scrubber likely decomposed following depletion (over-chlorination) of caustic soda (NaOH), releasing chlorine and possibly other toxic materials into the atmosphere. The CSB's research revealed a need for better guidance on the magnitude and duration of toxic releases that can occur in over-chlorination incidents. Such data will enable companies to properly size mitigation equipment and provide useful information to emergency responders.

Chlorine is commonly scrubbed with caustic soda (NaOH) solutions. The chlorine moves from the gas to the liquid phase and reacts with the caustic soda to form sodium hypochlorite (NaOCl–bleach) and sodium chloride (NaCl - common salt), in accordance with:

Reaction 1 $Cl_2 + 2\ NaOH \rightarrow NaOCl + NaCl + H_2O$ (bleach formation reaction)

Each pound of chlorine reacts with 1.13 pounds of NaOH, removing the NaOH from the circulating scrubber solution. Reaction 1 ceases when the NaOH is fully consumed. Any additional chlorine fed to the scrubber will not be captured and will be emitted to the atmosphere.

Depletion of NaOH also leads to the rapid decomposition of bleach to form sodium chlorate and salt (NaCl), in accordance with reaction 2 (Adams et. al., 1992). Commercial bleach solutions typically contain between 0.2-0.5 percent caustic to maintain stability, with the exact amount of caustic determined by customer specifications.

Reaction 2 $3\ NaOCl \rightarrow NaClO_3 + 2\ NaCl$ (overall decomposition reaction)

Reaction 2 is rapid at neutral pH and ambient temperature. The rate strongly depends on bleach concentration, implying an initially high rate of decomposition that slows sharply as the bleach concentration decreases.

The decomposition reaction proceeds through several steps in which significant amounts of hypochlorous acid (HOCl); chlorine monoxide (Cl_2O); and hydrochloric acid (HCl) occur as intermediate species; that is, these materials are both formed and consumed in the overall reaction. Hypochlorous acid and chlorine monoxide are toxic and may contribute to hazardous emissions during over-chlorination incidents.

Reaction 2 is exothermic (heat-producing) and increases the temperature of the over-chlorinated scrubber, further accelerating the decomposition rate. Decomposition eventually slows as the bleach is consumed, and may continue at a low rate for an extended period.

Most of the hydrochloric acid intermediate formed is expected to be consumed converting bleach to hypochlorous acid, in accordance with:

Reaction 3 $HCl + NaOCl \rightarrow HOCl + NaCl$ (intermediate step in decomposition reaction)

The hypochlorous acid formed then decomposes to stable chlorate plus additional hydrochloric acid in accordance with:

Reaction 4 $2\ HOCl + NaOCl \rightarrow NaClO_3 + HCl$ (hypochlorous acid decomposition reaction)

The hydrochloric acid formed in this reaction is then available to convert additional bleach to hypochlorous acid, continuing the decomposition of the bleach to sodium chlorate. However, the reduced pH caused by hydrochloric acid formation and accumulation creates the potential for chlorine gas formation through:

Reaction 5 $HOCl + HCl \rightarrow Cl_2 \uparrow + H_2O$ (chlorine gas formation)

The rate at which the pH changes during decomposition is not well documented, but is expected to remain at or above pH ≈ 2.0,[1] low enough to readily produce chlorine by Reaction 5. The chemical literature reviewed by the CSB does not address the amount of chlorine formed by this reaction in over-chlorination incidents. The CSB investigators estimate that as much as 1,920 pounds of chlorine may have been released at Glendale by this mechanism.

A parallel bleach decomposition reaction described in The Chlorine Institute's "Sodium Hypochlorite Manual Pamphlet 96" is:

Reaction 6 $$2\ NaOCl \rightarrow O_2 \uparrow + 2\ NaCl$$

Reaction 6 produces salt and gaseous oxygen as products. This decomposition reaction is enhanced at high temperatures and low pH, the conditions created in an over-chlorinated scrubber by reaction 2. It is thus possible that reaction 6 contributes to the decomposition of bleach in over-chlorination incidents. While the products of reaction 6 are not hazardous, the oxygen produced could act as a stripping gas, enhancing the emission of volatile toxic materials from the scrubber.

Raising the pH by adding adequate excess caustic to the solution is expected to interrupt both reactions 2 and 6, and to absorb any chlorine gas dissolved in the scrubber solution. Once an over-chlorination incident has begun, this is the only way to interrupt the decomposition reactions and stop toxic gas emissions.

Over-chlorination incidents, including the incident at DPC-Glendale, are described as causing considerable rumbling and shaking of the equipment involved. It is likely that this results from the

[1] This is based on expert testimony and the stability of the chlorate salt formed in the decomposition reaction. No data were found documenting the changes in pH during over-chlorination incidents.

formation of gaseous products and the rapid heating of the scrubber contents by decomposition reactions 2 and 6.

While the chemical pathways in bleach decomposition appear to be well understood, published data do not address the identities and quantities of the toxic materials emitted from over-chlorinated scrubbers, nor are changes in system temperature and pH described in detail. This information is needed by companies to size mitigation equipment and to provide accurate information to emergency responders during over-chlorination incidents.

Appendix C DPC – Glendale Incident Time Line

11/14/2003 - 2:00pm
Bleach Production Report
Excess Caustic 1.76%
ORP 480 mV

→

11/17/2003 - 6:00am
Shift starts

→

11/17/2003 - 7:00am
Bleach Production Report
Caustic 1.60%
ORP 490 mV

→

11/17/2003 - 8:30am
Begin chlorine transfer

→

11/17/2003 - 10:00am
Bleach Production Report
Caustic 1.18%
ORP 510 mV

→

11/17/2003 - 10:15am
First ORP Safety Meter Alarm
Acknowledged, chlorine continues to flow

→

11/17/2003 - 11:15am
Second ORP Safety Meter Alarm
Acknowledged, chlorine continues to flow, operator prepares to take sample

→

11/17/2003 - 11:30am
Chlorine release.
Emergency shutdown & site evacuation

→

11/17/2003 - 11:34 am
911 caller reports a chlorine leak, calling neighboring businesses to evacuate

→

11/17/2003 - 11:35am
First alarm - hazardous materials incident
18 emergency responder units dispatched (PD, FD)

→

11/17/2003 - 11:38
Initial responders on site (Phoenix Fire Dept)

→

11/17/2003 - 13:17
Evacuation message delivered to 4128 phones in the evacuation area in English, Spanish and TDD

→

11/17/2003 - 13:30
Chlorine levels of 2 ppm at 250 ft radius, 15 ppm at 150 ft radius 25-35+ ppm at fenceline.
Responders working to close valves

→

11/17/2003 - 14:12
DEQ Hazardous Air Response Team takes first sample at West Pasadena - reading less than 0.2 ppm

→

11/17/2003 - 15:49
DEQ below detection limit readings except at 600 ft perimeter

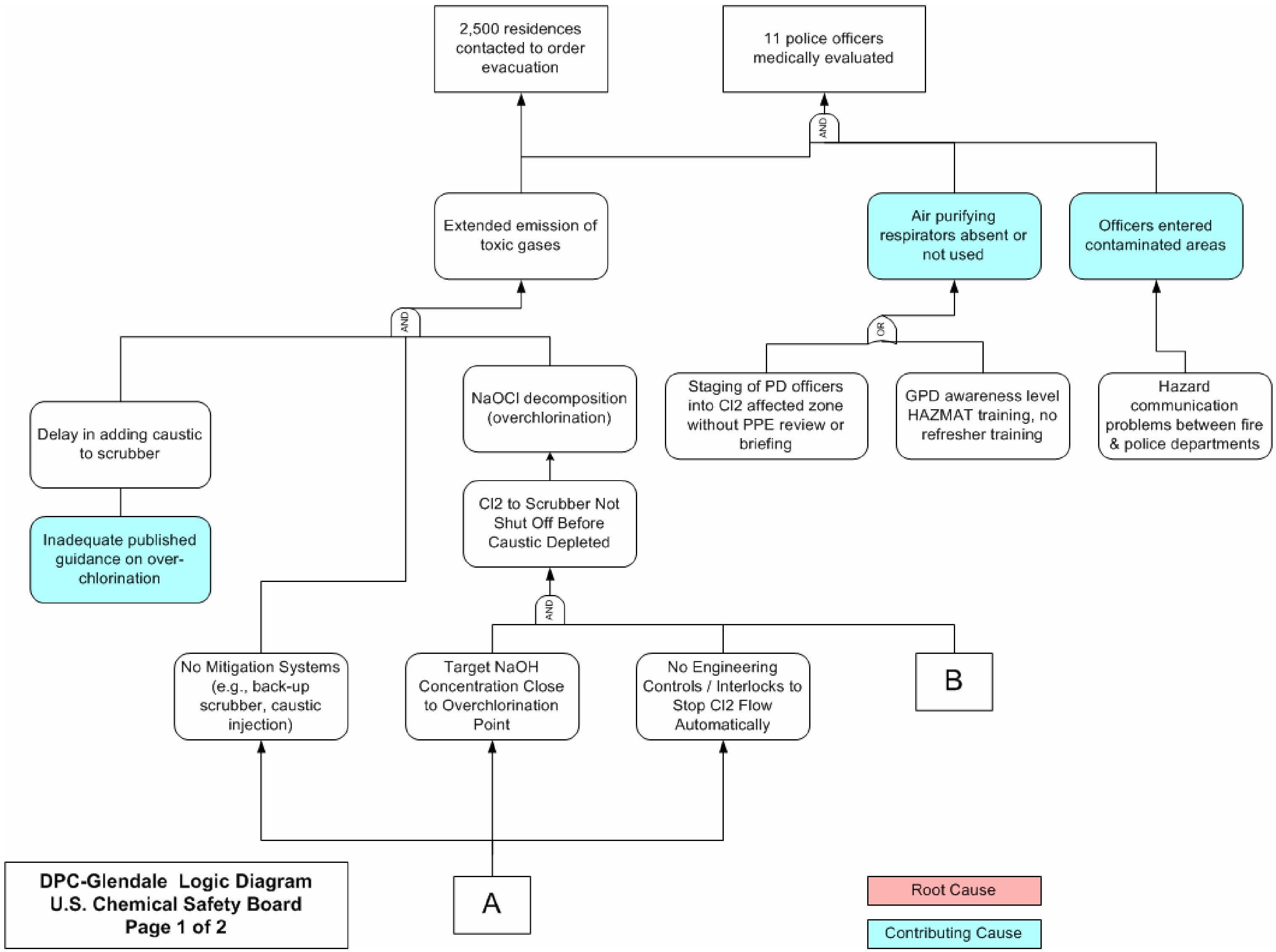
→

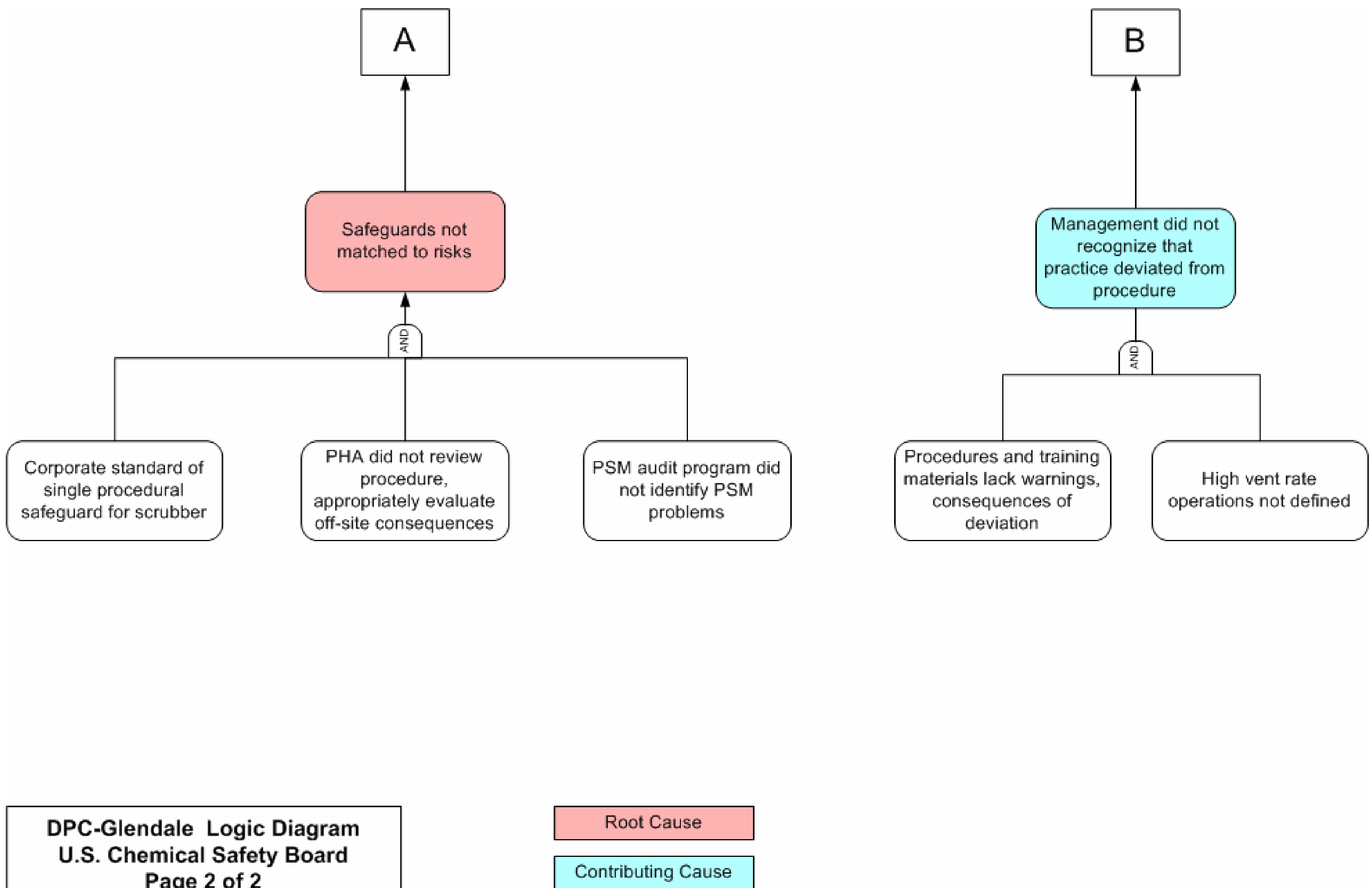
11/17/2003 - 17:30
DPC adds caustic to scrubber. DEQ reports brief emission.
Scrubber stabilized.

→

11/17/2003 - 20:54
Incident Closed by Glendale FD

Appendix D DPC – Glendale Incident Event Tree





DPC-Glendale Logic Diagram
U.S. Chemical Safety Board
Page 2 of 2