December 15, 2008

Mr. John Bresland
U.S. Chemical Safety and Hazard Investigation Board
2175 K Street, NW
Suite 650
Washington, DC 20037-1809

RE: CSB2004-02-I-AZ-R14
DPC Enterprises facility in Glendale, AZ on November 17, 2003

Dear Mr. Bresland:

This letter is the Chlorine Institute's ("Institute's" or "CI's") final response to Ms. Merritt's letter dated March 8, 2007. In that letter the Chemical Safety Board ("CSB") makes recommendations to CI as part of its final investigation report into the November 17, 2003 DPC Enterprises, Glendale, AZ incident. CI appreciates the opportunity to work with the CSB on matters related to the safe use and handling of chlorine. We believe the following information is an appropriate and comprehensive response.

In the CSB letter of March 8, the Institute is asked to consider the following:

1. Clarify the chemistry involved in over-chlorination incidents so that "Chlorine Scrubbing Systems, Pamphlet 89," and other pertinent publications: **2004-2-I-AZ-R14**
    - 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.

The remainder of this letter constitutes the Chlorine Institute's response to the CSB's recommendations cited above. Our response is broken into six parts each addressing a specific issue raised in the March 8 letter or the February 2007 final Investigation Report:

- Clarification of terminology;
- A review of previous activity;
- Changes to Chlorine Institute recommended practices and safeguards;
- Chemistry of overchlorination in a scrubber;
- Emergency response to an overchlorination event; and
- The CSB's implied recommendation for a minimum of 8% caustic (sodium hydroxide) for effective scrubber operation.

I. Terminology: Overchlorination versus Bleach Decomposition

The Institute would first like to note a minor point of clarification. In its recommendation the CSB uses the phrase "bleach decomposition." The Institute considers bleach decomposition to consist of those chemical reactions that "naturally" occur as bleach degrades over time, with the addition of no other substances and affected solely by temperature, initial bleach concentration, sunlight, presence of metal cations, etc. Decomposition chemistry is different from the chemistry associated with the overchlorination of a caustic scrubber solution. The Institute's response, as contained in this letter, addresses caustic scrubber overchlorination issues primarily associated with the manufacture of sodium hypochlorite (bleach).

II. Previous Institute Activity

In response to the incident The Chlorine Institute has already:

- Conducted a member survey on scrubbers. We received 190 responses to a comprehensive set of questions and reported compiled results to the CSB.
- Chartered a task group to review and update Pamphlet 89 – Chlorine Scrubbing Systems.
- Updated and revised Pamphlet 89 as follows:
    - The introduction was expanded to more clearly define the scope of the pamphlet and define those design issues not covered.
    - Section 2.6.1 was modified and Graph 2.1 was added to address concerns with the formation of solid salts, which can occur during chlorine absorption as well as from the presence of carbon dioxide.
    - New graphs were added to Section 3 that assist the reader in understanding effluent temperature at various chlorine conditions and caustic strength.
    - Section 4.9 on reliability was added.
    - Appendix A, which formerly contained Data Sheet A-1 on chlorine properties, was replaced with a calculation procedure for chlorine absorption unit design. The chlorine properties can be found in other CI documents.
    - Various minor editorial and formatting changes were also made throughout the document.
- Edition 3 of Pamphlet 89 was published in August 2006.
- Forwarded a copy of the third edition of Pamphlet 89 to the CSB's Jordan Barab in January 2007.
- Held a meeting with the CSB to discuss the investigation's preliminary recommendations on January 19, 2007.

This activity was previously documented in an Institute letter to the CSB dated May 3, 2007.

III. Changes to Chlorine Institute Recommended Practices and Safeguards

This section responds to the CSB's recommendation that the Institute's pamphlets

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

The Chlorine Institute, through its Issue Team and Task Group process has reviewed the existing technical guidance found in Institute pamphlets. It has been determined that modifications to the following CI Pamphlets are appropriate.

- Pamphlet 64 – Emergency Response Plans for Chlor-Alkali, Sodium Hypochlorite, and Hydrogen Chloride Facilities, Edition 6, February 2006
- Pamphlet 89 – Chlorine Scrubbing Systems, Edition 3, August 2006
- Pamphlet 96 – Sodium Hypochlorite Manual, Edition 3, April 2006

In general these changes focus on:

- Ensuring that process overchlorination is included as a possible incident in a facility's emergency response planning;
- Informing users that the overchlorination of a scrubber can release significant amounts of chlorine and that an overchlorinated scrubber could continue to release chlorine until mitigation measures modify certain reactor conditions or the pH increases (e.g. through the addition of caustic);
- Proper operation of emergency scrubber units; and
- Analysis of the risks associated with the production of sodium hypochlorite and implementation of the proper type and number of layers of protection to prevent a release.

A summary of the changes are as follows:

<u>Pamphlet 64</u>

- Revised Section 2.4 - Planning for Different Types of Emergencies to include suggestions for inclusion of specific events in a facility's emergency response plan, including overchlorination events.
- Revised Section 2.5 - Scope of the Emergency to emphasize the need to scope all potential emergencies, releases and responses.
- Also see Part V of this letter below.

<u>Pamphlet 89</u>

- Revised Section 2.4 - Overchlorination:
    - Assume that once the caustic in a scrubber solution is consumed, ALL chlorine entering the scrubber will vent from the scrubber; and
    - Recognize that as chlorine continues to feed to the chlorine saturated solution the solution pH will decrease via acid generation. Once chlorine flow is stopped to the

overchlorinated solution, chlorine will continue to evolve from the solution until enough HCl is consumed to increase the pH above 5.

- Revised Section 4.9 - Reliability
    - Understand that no matter the type of scrubbing system employed, sufficient caustic should always be available to neutralize chlorine. A "sufficient" amount of caustic is based on the time required to safely stop chlorine flow to the scrubber in an upset situation;
    - It is recommended that at least one redundant layer of protection for scrubbing chlorine be in place and that at least one online measurement system should continuously monitor the effectiveness/ability of the system to neutralize chlorine; and
    - Special consideration should be given to containing and routing the vents from chlorine scrubbing or bleach manufacturing systems that regularly operate at low caustic levels.
- Also see Part IV of this letter below.

<u>Pamphlet 96</u>

- Revised Section 2.4 – Aqueous Chemistry to remind the reader that if the concentration of elemental chlorine exceeds its solubility at any temperature, chlorine gas will be liberated from the solution.
- Revised Section 4.3.5 – Overchlorination Protection:
    - Renamed section (originally named Emergency Scrubber Systems) to emphasize the primary intent of the discussion.
    - Discussed possible causes of scrubber overchlorination and/or breakthrough during the manufacturing of sodium hypochlorite;
    - Listed possible methods that manufacturers should consider to protect employees and the environment from the effects of a chlorine release during the manufacture of sodium hypochlorite, including a combination of both preventative and mitigation measures (i.e. layers of protection).
    - Emphasized that mitigation equipment should be considered exclusive for emergencies. If not, the risks associated with use of this equipment in the regular manufacturing processes should be carefully studied using appropriate hazard analysis methodology.

Changes to each pamphlet have been approved and updated documents will be available in the on-line CI library by the end of the calendar year.

IV. Chemistry of Overchlorination in a Scrubber

This section responds to the CSB's recommendation that the Institute

> . . . clarify the chemistry involved in over-chlorination incidents.

The Institute believes the chemistry involved in an overchlorination incident, though not completely documented, is well enough understood to address the necessary and important issues. That is, the chlor-alkali industry knows enough about a bleach manufacturing or scrubber overchlorination incident to properly prevent an occurrence, respond to and end an incident, and mitigate the facility and community impacts. The Institute believes that Section 2.4 of Pamphlet 89 (as amended) provides all the information necessary. Section 2.4, as amended, is reprinted below.

2.4 Overchlorination

2.4.1 The importance of excess sodium hydroxide to avoid overchlorination cannot be overstated. As chlorine is continuously fed to a solution containing no caustic the solution becomes saturated with chlorine (between 0.002 and 0.02 pounds/gallon depending on pH, temperature, and ion concentrations). Once the solution is saturated with chlorine, chlorine will start venting from the scrubber. In general it should be assumed that once the caustic is consumed in the solution, ALL chlorine entering the scrubber will vent from the scrubber.

2.4.2 Additionally as chlorine continues to feed to the chlorine saturated solution the solution pH will decrease via acid generation from the following reactions:

$$NaOCl + Cl_2 + H_2O \rightarrow 2HOCl + NaCl$$

$$Cl2 + H2O \leftrightarrow HOCl + HCl$$

2.4.3 As the pH drops below 11 the following reaction takes place continuing to lower the pH via the formation of additional HCl:

$$2HOCl + NaOCl \rightarrow NaClO_3 + 2HCl$$

2.4.4 As the pH drops below 5 the HOCl starts to decompose to HCl via the following reaction:

$$2HOCl \rightarrow 2HCl + O2$$

2.4.5 Once enough HCl is generated chlorine will be released from the solution via the following reaction:

$$HOCl + HCl \leftrightarrow H2O + Cl2$$

2.4.6 Once chlorine flow is stopped to the overchlorinated solution, chlorine will continue to evolve from the solution via the above reaction until enough HCl is consumed to increase the pH above 5.

V. Emergency Response to an Overchlorination Event

This section responds to the CSB's recommendation that the Institute

> . . . 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.

Users of chlorine (e.g. bleach manufacturing) should discuss in their facility emergency response plans how to deal with an accidental overchlorination of a process (e.g. overchlorination of a bleach reactor). The plan should include the following:

- A means of detection of the overchlorination event;
- An estimate of the affected area both within the plant and outside the facility (CI Pamphlet 74 provides guidance);
- An announcement process to warn the on-site workers of the event and to communicate their expected action;
- A means to notify the local authorities to allow them to take action on sheltering in place or evacuating the impacted area;
- A defined plan to stop the overchlorination of the process (block in the chlorine);
- A defined plan to implement mitigation measures to halt the release of chlorine from a oversaturated reactor (e.g. raising the pH of the solution in a bleach reactor); and
- The plan should be tested annually.

This information will be transmitted to interested parties through modifications to Pamphlet 64.

VI. The CSB's Implied Recommendation for a Minimum of 8% Caustic for Effective Scrubber Operation

This section responds to Section 2.3.2 Scrubber Operation (the bottom of page 15 and the top of page 16) of the final investigation report (February 2007) where the Board discusses "scrubbing efficiency is best at caustic concentrations above 8 percent[.]" CI disagrees with the statement that eight percent or higher is the most efficient caustic concentration. The Institute believes that the CSB is confusing the different but related issues of "scrubbing efficiency" and "safe scrubber operation."

First, it should be clearly understood that the Institute agrees with the Board's discussion found in the partial paragraph found at the top of page 16.

> . . . operating the scrubbers simultaneously as critical safety devices and as batch bleach production units requires great care . . .

Every facility has its own unique characteristics that affect its equipment choices and operational procedures. A facility which chooses to simultaneously operate a scrubber as both a safety device and bleach unit will have its own unique operational concerns. The facility must conduct a thorough process safety analysis of the unit and implement the proper layers of protection to prevent overchlorination and a chlorine release to the atmosphere.

With regard to the eight percent statement, Institute member testing and experience have shown that:

- For tower type scrubbers that inject chlorine and caustic and rely on chlorine gas and caustic in solution to come into contact with each other (e.g. spray towers, packed towers), caustic solutions below 8 wt% sodium hydroxide have less than 100% scrubbing efficiency when the stoichiometric ratio of sodium hydroxide to chlorine approaches 1.
- For scrubbers where the chorine gas will always thoroughly contact the caustic solution (e.g. sparge tanks with properly designed and operated spargers or eductors), as long as there is a stoichiometricly sufficient mass of caustic in the solution to neutralize the worse case amount mass of chlorine that may enter the scrubber, the scrubber can be designed to achieve total chlorine removal with solution concentrations down to 1 wt% or less.

The Institute hopes this clarifies its concerns. Low caustic concentrations can be effectively used in scrubbers as long as the proper safety precautions are implemented.

VII. Conclusion

The Chlorine Institute is recognized as the chlor-alkali industry’s premier safety and technical organization. The Institute’s mission is to promote safety and the protection of human health and the environment in the manufacture, distribution, and use of chlorine. This includes a long-term goal of zero injuries and releases. We appreciate the opportunity to work with the CSB on this issue and to continue our efforts to make the chlor-alkali industry one of the safest.

As discussed above CI has incorporated the concerns and issues raised by the Glendale incident into its technical guidance and recommendations. Scrubber and process overchlorination has been and will always be part of the Institute’s process safety considerations. The Institute considers this document its final deliverable in response to the CSB recommendations found in its March 8, 2007 letter. The Institute assumes that no additional response will be necessary unless requested in writing by the CSB.

David Dunlap, CI’s Vice President for Health, Environment, Safety and Security (HESS), is the Institute’s lead staffer for this issue. Please contact David (direct 703-741-5765) or me (direct 703-741-5764) if there are questions or concerns.

Regards,

Arthur E. Dungan
President

cc: Rachael Gunaratnam, CSB
David Dunlap