Assessment Report Goes to Press

During the fifteen years that have passed since the tragic accident in Bhopal, India, many organizations throughout the United States, including industry, government at all levels, trade associations, labor organizations, environment and public interest organizations, and universities, have taken major steps toward improving response, preparedness, and prevention of chemical incidents. However, to date there has not been a way to assess whether the myriad of activities are really improving chemical safety.

In an effort to begin to answer this complex question, the Mary Kay O’Connor Process Safety Center launched the National Chemical Safety Program. This program began with a Roundtable meeting of diverse stakeholders in June 1999, to identify the nation’s chemical safety goals. Through collaborative efforts, the Roundtable established the National Chemical Safety Goal as:

*Chemical incidents are zero; chemical enterprises have earned the public’s trust; and public, government, and facility interactions improve safety and reduce risks.*

Out of this collaboration, the Center undertook a National Chemical Safety Assessment project to conduct an assessment of chemical safety and a survey of public trust. This first annual assessment report looks at these two aspects and begins to measure progress toward reaching the National Goal.

The primary focus of this report is to assess the status of chemical safety and public trust in the United States. Specifically, the National Chemical Safety Assessment report:

- Assesses the adequacy and scope of currently available data sources regarding chemical incidents;
- Identifies trends and consequences in chemical incidents, fatalities, and injuries;
- Surveys residents near chemical facilities to gauge their level of knowledge and trust; and
- Presents suggestions that can be used to improve chemical safety.

(Report continued on page 13)
We, at the Mary Kay O’Connor Process Safety Center appreciate the support and assistance given to us by various organizations and individuals. This support comes in many forms without which many of the activities of the Center would not be possible. A major part of the support for various programs and activities of the Center comes from annual membership dues. Organizations can become members of the Center at the Partner, Sponsor, or Advisor level. Small business and individual memberships are also available. Details about membership benefits, membership criteria, and annual dues are available on request.

The Chemical Safety Assessment Project is moving ahead with renewed vigor and direction. The first Annual Chemical Safety Assessment Report is going to the press as scheduled in the near future. Also, with the addition of Bill Effron as the Associate Director with primary responsibility for the Assessment Project, things are beginning to take off at a much higher pace. In the near future, we intend to complete the hiring process for other critical personnel including a Repository Manager and Data Analysts. As we move through these critical milestones, we would like to call on the support of the Roundtable and all stakeholders.

Other research activities of the Center are also in full bloom. Our reactive chemicals research has resulted in several publications. This includes experimental work on hydroxylamine and family of hydroxylamine compounds. Our goal in the reactive chemicals research arena is to combine experimental and theoretical understanding of reactive chemical analyses to develop a structured approach for reactive chemical hazard management. In the aerosol research, we have completed two years of data collection on aerosol generation. The work has resulted in the publication of much needed aerosol data for heat transfer fluids. Currently, work is continuing on additional data gathering on an array of other fluids. The next phase of the aerosol research will concentrate on flammability studies. The objective is to be able to use the experimental data to further the understanding of aerosol generation mechanism for heat transfer fluids and other high flash point fluids. The advanced understanding will be used to develop aerosol correlations, determine design solutions to avoid hazardous situations, and identify potential inhibitors to prevent aerosol formation. Research is also moving ahead in other areas of interest for the Center. These include inherently safer design, abnormal situation management, quantitative risk assessment, benchmarking and measurement systems, and electrostatics.

The 2001 Symposium is also fast approaching. The program has been finalized and once again we expect two days of intense discussions and presentations on technical issues of interest in the process safety arena. We look forward to seeing you all at the Symposium on October 30-31, 2001 at the Reed Arena in College Station, Texas.

M. Sam Mannan
The National Chemical Safety Program Roundtable met at Reed Arena in College Station on July 31 and August 1, 2001. The participants listened to several presentations on the work having been performed by the Center over the past several months. Dr. Sam Mannan refreshed the mission and goals of the Center and of the Assessment project to the group in his opening presentation on Tuesday afternoon. There have been several issues advanced during the development of the report. Dr. Mannan stressed the need for the Roundtable to help resolve the issues before concluding the meeting.

The presentation by Mr. Bill Effron on the Metrics for Chemical Incidents in the United States developed a number of interesting discussion points among the various stakeholders. The topics covered included the data sources selected, the quality of the data reviewed, and the resulting observations. The group learned of the difficulties in trying to consistently review data from various data sources, which in some cases was created for very different purposes. For example: the NRC collects incident reports on spills, while the EPA 5-year incident data looks at very different chemical substances. The variety of definitions used by the various agencies only compounds the level of complexity involved in measuring progress.

Mr. Mike O’Connor expanded on these difficulties in his presentation on the Patterns, Causes and Consequences of Chemical Incidents. The differences in the purposes of the databases underscore the importance of understanding not only their purpose but also their limitations. While observations can be drawn from the individual sources, the Center must be careful not to draw too broad a conclusion from any one source. The stakeholders discussed using one or two data sources and building on existing information; but soon realized that the subsequent analyses would be limited by the quality and completeness of the basic data.

The Public Trust and Community Interaction presentation by Dr. Mannan led to a number of questions from stakeholders. The questions and answers after the presentation helped the group to better understand the information gathered. A need to continually communicate information to those potentially affected was one of several findings. The survey involved over 700 randomly selected households that are within one mile of a chemical facility. The facilities were also randomly selected from the EPA’s 5-Year Accident History database.

Mr. Alan Webber of the Marasco Newton Group presented a session on developing metrics from primary and secondary data sources. Mr. Pete Macias, also of Marasco Newton outlined the basics of a communication plan for the Assessment Report once it is completed. Each sought input from the stakeholders related to items of significance and target audiences.

Mr. Bill Effron led a discussion on the vision of the National Chemical Incident Repository. The repository would involve delivering information to the various stakeholder groups via a World Wide Web interface. An example would be for an individual citizen to input their zip code and receive a snapshot of chemical safety in their vicinity. That view might include the number of chemical facilities, the number and types of incidents involving certain regulated chemicals. The ability to search information could be expanded to include, e.g. injuries, as the both Center and stakeholders feel the quality of the data is acceptable for public distribution.

Both days of the Roundtable ended with open discussions involving each of the stakeholders. The results were recorded to assist in directing the Center as they complete the first National Chemical Safety Assessment Report. One stakeholder remarked, “This is the only place I know of that this diverse array of stakeholders comes together to discuss how to reduce chemical incidents and increase public trust.”
Center Relocates to Richardson Building

Over the past few weeks, the Mary Kay O'Connor Process Safety Center has relocated to the 9th and 10th floors in the Richardson Petroleum Engineering Building. The offices will be the home of the Director and the Associate Director, as well as all other Center employees. The software laboratory, library, and the National Chemical Safety Program research will make their homes in the new offices as well.

Bill Effron said, “It is wonderful to have the major components of the Center together under one roof. The research lab will however remain in Zachry due to their physical complexity and need for utilities such as dedicated ventilation hoods.”

The Center’s phone number will remain 979/845-3489 and the fax is 979/485-1493. Take a few moments the next time you are in College Station and visit the new headquarters of the Mary Kay O’Connor Process Safety Center in the Richardson Petroleum Engineering Building.

Donations Sought for Center Library

The Center Library is seeking donations of reference materials related to process safety. Materials of all ages and type are being sought. In some cases, older material may be more valuable to our researchers because it is rare or it helps explain the basis for a present practice that is not documented. Results of experimental research are very desirable. Also consider donating out of date industry standards from your corporate library. Symposium proceedings are especially useful since they typically have limited distribution.

Estate gifts may also be made and are welcome. This type of planned gift can be coordinated and arrangements made through the Texas Engineering Experiment Station (TEES) Development Office. Please contact Mary Cass at 979-458-1863 or at mary-cass@tamu.edu to make arrangements for your donation. The Center reserves the right to relocate material not suited for the library when appropriate. Please do not donate material with confidential or proprietary information without a release from a person legally authorized to do so.

Donations to the Center are tax deductible (to the extent allowed by law). The donor will be responsible for a 3rd party appraisal to determine the value. Receipts issued by the TEES Development Office would confirm receipt of donation, however, the amount would not be declared because the donation is considered a non-cash gift.
SAFETY ALERT:
Explosive Gas and Dust

The Mine Safety and Health Administration (MSHA) reports that during the past 5 months, eight explosions have occurred at metal/nonmetal mining operations. These accidents resulted in one fatality and nine nonfatal injuries. MSHA believes each of these accidents could have been prevented. MSHA is requesting that mine operators reevaluate all work procedures now in place regarding handling, storage or use of explosive fuels or dust. The following is a brief synopsis addressing each event gleaned from the preliminary information reported to MSHA. This information is not intended to replace the investigation findings pertaining to these accidents.

- February 7, 2001- An explosion occurred in the dust collector for the pulverized coal fuel system at a cement operation in Virginia. Temperature spikes reached 170 degrees Fahrenheit, which indicated problems in the coal grinding mill. Subsequently, hot embers were transported from the coal mill through the cyclone into the dust collector bag house where they initiated the explosion.

- February 8, 2001- An explosion occurred in the kiln at a cement operation in Pennsylvania. Two natural gas lines were lit and inserted into the kiln during the pre-heat, start-up procedure. After it was determined that the flames appeared to be extinguished, one of the lines was removed and relit. As the line was being reinserted into the kiln, it ignited the accumulation of gas.

- March 20, 2001- An explosion occurred inside an enclosed weigh scale sump at a crushed stone operation in Wisconsin. A lit, hand-held propane torch had been placed inside the sump to thaw a build up of ice. The flame extinguished, allowing an explosive mixture of gases to accumulate. When a second lit torch was placed in the sump, it ignited the explosive gases.

- April 2, 2001- An explosion occurred in the coal grinding mill at a cement operation in Alabama. The explosion, which was initiated by hot embers generated in the coal mill, damaged the grinding mill, the cyclone and the duct work of the pulverized coal feed system.

- May 3, 2001- An explosion occurred in a transfer chute at a cement operation in California. The access door had been opened and a miner was removing built-up material with an air lance. It is believed that the metal-to-metal contact generated by the air lance on the side of the chute provided the ignition source that ignited the coal dust.

- May 19, 2001- An explosion occurred in a kiln at a clay operation in Texas. The kiln had been taken off-line and several repairmen had entered it to perform maintenance. As the repair was being done, an accumulation of organic dust fell and traveled through the piping into the combustion chamber where it was ignited by hot material.

- May 30, 2001- An explosion occurred in the storage bin of the indirect fired, pulverized coal feed system at a cement plant in Virginia. A fire was detected in the bin and carbon dioxide was introduced into the closed system. The coal feed was stopped and the bin was emptied. When the coal feed was restarted, hot embers remaining in the bin ignited the coal dust.

- May 31, 2001- An explosion occurred in a kiln at a cement operation in Missouri. Propane was being used to pre-heat the kiln during the start-up procedure. The flame extinguished and the kiln filled with gas, which was subsequently ignited.

DISCLAIMER

This alert is being provided by the Mary Kay O’Connor Process Safety Center as a service. Users of this information should make appropriate analysis and check the information to their own satisfaction. The Center does not warrant or represent, expressly or implied, the correctness or accuracy of the content or the information presented in this alert, nor can they accept liability or responsibility whatsoever for the consequences of its use or misuse by anyone.
Titanium has been involved in a spate of incidents recently resulting in significant damages from fires. Although the hazards of titanium fires have been documented to some extent, these recent incidents provide additional information about the hazards and consequences that may not have been known earlier. The two incidents presented below provide examples of titanium fire-related hazards and consequences.

**INCIDENT 1: A FIRE IN TITANIUM-STRUCTURED PACKING INVOLVING THERMITE REACTIONS**

In a recent incident at a chemical plant, two beds of titanium structured packing in a distillation tower ignited. Ignition occurred while a hand held battery powered grinder was in use as part of an inspection activity. Sparks formed when the grinder touched stainless steel or titanium are believed to have initiated a thermite reaction between the thin sheet titanium structured packing and a dried iron oxide layer that had accumulated on the packing surfaces.

There were no fatalities or serious injuries associated with this incident. The metal fire caused extensive damage to the bottom head of the vessel as well as various internal components located in the lower portion of the tower. Replacement of the lower section of the vessel and all of the beds of structured packing was required.

Samples of the packing had been removed before the fire. Inspection and testing of this material after the incident confirmed both the existence of the iron oxide layer and its ability to sustain a propagating thermite reaction with the underlying thin sheet titanium.

**Description of Tower**

The tower, which is rated above 20 bar, included multiple beds of structured packing manufactured from grade 2 titanium. Other internal components, such as liquid distribution troughs and rings and support structures, were also constructed from grade 2 titanium. The structured packing is assembled from 0.1 mm thick corrugated titanium sheets fastened together to form bundles. Individual bundles are stacked vertically and horizontally (edge up) to produce a bed of the desired diameter and depth.

**The Event**

The unit was down for repair/inspection, and had been opened and prepared for entry using established plant procedures. Personnel noted a dark coating (including some rust colored streaking) adhering to the structured packing surfaces. Samples of the coated packing from the beds were taken to assess corrosion and verify materials of construction. The coating did not appear to contain any organic material.

After completing entry and hot work procedures per the site’s established policies, inspectors carried a hand held battery powered grinder into the tower between the bottom two beds. They planned to utilize a materials identification screening procedure (see NFPA 481, Appendix B) that involved passing the rotating grinding wheel lightly and quickly across the surface of components being checked and noting the characteristics of the sparks generated.
The inspector started testing individual bundles with the grinder. During this activity he noticed a small localized orange glow originating down inside the packing structure of the bottom bed. The glow occurred in an area towards which sparks had previously traveled. About that same time, a very faint white cloud/fog was observed rising through one of the structured packing channels. The inspector alerted the crew to a possible fire, and he and the attending operator quickly moved towards the manway. Within an estimated 30-45 seconds, the orange glow had turned into a brilliant white area about ½ meter in diameter and was spreading through the bed at a rapid rate. The entire bed had become brilliant white as the inspector exited the tower.

Emergency alarms were activated, and within 12-14 minutes personnel started water flowing into the tower via an overhead reflux line in an attempt to extinguish the metal fire. Data retrieved later indicated that temperatures exceeded 600 deg C (the maximum range of the thermal measurement) at several locations around the two beds within 2 minutes from the start of the fire. The data also suggested that the support structure of the bed located above the work area failed, causing it to collapse onto the lower bed. Temperatures in the bottom section of the tower started falling approximately 4-6 minutes after water was added to the top of the tower. The entire fire event was over within 23-24 minutes from the time the orange glow was detected.

Explosive noises occurred within the opened tower after the water reflux was started. Cause of the noises is not known but they may have resulted from rapid vaporization of water, release and subsequent ignition of hydrogen (which is generated by the reaction of hot titanium and steam), or both. The vessel, which was designed for pressures well above atmospheric, did not appear to suffer additional damage from these occurrences. The initial “steam” or “smoke” exiting all manways on the tower was initially a brownish-red, rust color, but this quickly became a white cloud.

The burning, molten mass of titanium, including its combustion products, melted through additional structures in the tower and migrated to the bottom. A hole melted through the bottom head and allowed portions of the molten metal to fall into tower support skirt where it continued to burn. Brilliant white sparks (consistent with burning titanium) and molten metal slugs were expelled from the bottom manways and the openings in the support skirt. These sparks and slugs traveled 30-50 meters.

In addition to starting water flow through the reflux line, emergency response personnel directed water from various firewater turrets onto the outside of the tower shell, tower skirt, and adjacent equipment for cooling. Also, they attempted to spray water into the lower tower manways. Within 23 minutes the thin sheet titanium packing material in the two beds was consumed and the fire ceased. It is believed that the metal fire self extinguished when the thin sheet material was consumed.

Internal inspection of the tower revealed significant damage to the lower section of the tower. The two titanium beds were consumed and there was extensive damage to internal structures such as support grids, liquid distribution troughs, support rings, etc. In addition, a 150mm diameter hole through the bottom of the tower was found. The evidence indicated that titanium metal combustion was largely limited to the thin packing sheets. Thicker, more massive components such as bed support structures and distributor troughs appeared to experience little or no direct combustion, though these components suffered significant damage from the heat.

**Background on Titanium Fires**

Prior to this incident, a considerable amount of literature existed on titanium burning in oxygen enriched atmospheres using test specimens that were thicker than the thin sheets used to construct the structured packing. This earlier work, by itself, suggested that clean titanium would not propagate sustained burning.
in air at atmospheric pressure. Previously reported fires with titanium structured packing tended to involve supplementary fuels such as combustible organic deposits and/or pyrophoric materials (e.g., iron sulfide). However, the reported testing was not designed to address the effects of very thin components or thermite reactions with iron oxide.

A “thermite” reaction can occur between a metal oxide and another metal that has a greater affinity for oxygen. When iron oxide and titanium metal are involved, the products of the reaction are titanium oxide, elemental iron, and a large exothermic heat of reaction. If the reaction occurs in an oxidizing environment, the iron may “burn” to iron oxide, a process that releases additional heat as well as regenerates the iron oxide to perpetuate the thermite reaction.

Little systematic work has been reported on thermite reactions involving titanium and iron oxide. Prior to this incident, there had been a small number of reported cases in which titanium combustion occurred in air in the presence of significant quantities of iron oxide. However, these incidents generally involved welding, torch cutting, or other situations where very high temperatures or high energy densities were applied to titanium/iron oxide.

Post-Fire Analysis of Recovered Samples

Tests and examinations of the iron oxide coated packing samples recovered before the fire indicated the coating was mainly iron oxide. No organic materials were detected. The thickness of the coating ranged from 2.5 to 25 microns with significant portions of the samples averaging 15-25 microns. The coating could best be described as adhering loosely rather than tenaciously.

After the tower was repaired and placed back in service, investigations confirmed that soluble iron would precipitate as Fe₂O₃ in the tower and adhere to the packing surface. Significant accumulation was observed to occur within a few months with an average soluble iron concentration of less than 1 ppm in the tower liquid.

Ignition Studies on Thin Sheets

After the incident, studies were conducted on (1) new “clean” samples of 0.1 mm thick titanium packing; (2) samples with very thin iron oxide coatings; and (3) samples from the tower with 15 – 25 micron thick coatings of iron oxide. (Note: Testing was done at a facility in New Mexico, where the local atmospheric pressure averages 12.4 psia.) Some observations include:

- Clean samples of 0.1 mm thick titanium would not sustain combustion at local atmospheric pressure unless the air was significantly enriched with oxygen.
- Samples with thin iron oxide coatings (1 – 2 microns) behaved in a manner indistinguishable from clean titanium.
- Under test conditions, samples with a 15 – 25 micron iron oxide layer required a slight amount of oxygen enrichment to undergo self-sustained combustion at the local atmospheric pressure at the test facility.
- At elevated test pressures, self-sustaining “combustion” of the 15 – 25 micron coated material occurred in pure nitrogen.
Mary Kay O’Connor Process Safety Center

BEYOND REGULATORY COMPLIANCE, MAKING SAFETY SECOND NATURE

October 30-31, 2001

Reed Arena • Texas A&M University
College Station, Texas

Early Registration Deadline is October 1, 2001

http://process-safety.tamu.edu
### Time Table

**Tuesday, October 30, 2001**

<table>
<thead>
<tr>
<th>Time</th>
<th>Track I</th>
<th>Track II</th>
<th>Track III</th>
</tr>
</thead>
</table>
| 8:15 - 9:45AM    | 8:15AM - General Session  
"Some Problems and Opportunities That Have Been Overlooked"  
Tutorial and Discussion led by Dr. Trevor Kletz | 9:30AM - State of the Center  
Research Program, Current Activities, and Future Direction  
Dr. Sam Mannan, Director, Mary Kay O’Connor Process Safety Center |                                                                 |
|                  | **Track I**                                                            | **Track II**                                                             | **Track III**                                                            |
|                  | Benchmarking and Measurement Systems                                     | Reactive Chemicals - I                                                   | Risk Assessment/  
Risk Management - I                                                      |
| 10:15 - 11:45AM | Process Management for Safety                                           | Reactive Chemicals - II                                                  | Risk Assessment/  
Risk Management - II                                                      |
| 11:00 - 12:30PM | Economics-101 of PSM Systems                                            | Reactive Chemicals - III                                                 | Risk Assessment/  
Risk Management - III                                                      |
<p>| 3:00 - 4:30PM    |                                                                 |                                                                 |                                                                 |
| 5:00-7:00PM      | 5:00-7:00PM Cocktails Reception                                         |                                                                 |                                                                 |</p>
<table>
<thead>
<tr>
<th>Time</th>
<th>Wednesday, October 31, 2001</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:15 - 9:45AM</td>
<td>General Session</td>
</tr>
<tr>
<td></td>
<td>National Chemical Safety Program -- 2001 Chemical Safety Assessment Report</td>
</tr>
<tr>
<td></td>
<td>• A Report on Chemical Safety in the US</td>
</tr>
<tr>
<td></td>
<td>• Survey of Public Trust and Community Interaction</td>
</tr>
<tr>
<td></td>
<td>• Future Direction</td>
</tr>
<tr>
<td>10:15 - 11:45AM</td>
<td>Track I</td>
</tr>
<tr>
<td></td>
<td>Chairs: David Chung and Skip Early</td>
</tr>
<tr>
<td></td>
<td>Safety Instrumented Systems</td>
</tr>
<tr>
<td></td>
<td>• “Expanding the Applicability of ISA TR84.02 in the Field,” L. Beckman, HIMA-Americas, Inc.</td>
</tr>
<tr>
<td></td>
<td>• “Safe Automation Gap,” A.E. Summers, SIS-Tech Solutions, Inc.</td>
</tr>
<tr>
<td>10:15 - 11:45AM</td>
<td>Track II</td>
</tr>
<tr>
<td></td>
<td>Chairs: Chap Pierce and Rob Smith</td>
</tr>
<tr>
<td></td>
<td>Aerosols and Release Modeling</td>
</tr>
<tr>
<td></td>
<td>• “Modeling Aerosol Rainout,” T. Spicer and J. Havens, University of Arkansas</td>
</tr>
<tr>
<td></td>
<td>• “Understanding the Formation of Heat Transfer Fluid Aerosols in Air,” K. Krishna, T-K. Kim, K.D. Khim, W.J. Rogers, and M.S. Mannan, MKOPSC</td>
</tr>
<tr>
<td>10:15 - 11:45AM</td>
<td>Track III</td>
</tr>
<tr>
<td></td>
<td>Chairs: Kathy Shell and Simon Schubach</td>
</tr>
<tr>
<td></td>
<td>Case Histories/Case Studies</td>
</tr>
<tr>
<td></td>
<td>• “Picture This! Incidents That Could Happen in Your Plant,” R.E. Sanders, PPG Industries</td>
</tr>
<tr>
<td></td>
<td>• “Analysis of an LPG Explosion and Fire,” T.V. Rodante, ECRC</td>
</tr>
<tr>
<td>1:00 - 2:30PM</td>
<td>Track I</td>
</tr>
<tr>
<td></td>
<td>Chairs: David Chung and Skip Early</td>
</tr>
<tr>
<td></td>
<td>Emergency Response and Community Interaction</td>
</tr>
<tr>
<td></td>
<td>• “The Role of Community Advisory Panels in the Aftermath of Critical Incidents in the Chemical Processing Industry,” M. Dore, Lowenstein Sandler PC</td>
</tr>
<tr>
<td></td>
<td>• “Handling a Crisis Situation Through Media Training,” P. Macias and D. Barton, Marasco-Newton Group, Ltd.</td>
</tr>
<tr>
<td></td>
<td>• “Use of Surveys for Emergency Communications,” R. Deville, Harris, Deville, &amp; Associates</td>
</tr>
<tr>
<td>1:00 - 2:30PM</td>
<td>Track II</td>
</tr>
<tr>
<td></td>
<td>Chairs: Chap Pierce and Rob Smith</td>
</tr>
<tr>
<td></td>
<td>Explosion Modeling and Mitigation</td>
</tr>
<tr>
<td></td>
<td>• “Explosion Risk Assessment, How the Results Vary With the Approach Chosen,” O.R. Hansen and J.R. Bakke, GexCon</td>
</tr>
<tr>
<td></td>
<td>• “A Comparison of Simple Vapor Cloud Explosion Methodologies,” G.A. Fitzgerald, EQE International</td>
</tr>
<tr>
<td></td>
<td>• “An Inherent Technology to Mitigate Vapor Cloud Explosions,” D.G. Clark, DuPont</td>
</tr>
<tr>
<td>3:00 - 4:30PM</td>
<td>Track III</td>
</tr>
<tr>
<td></td>
<td>Chairs: Kathy Shell and Simon Schubach</td>
</tr>
<tr>
<td></td>
<td>Benchmarking PSM Program Components</td>
</tr>
</tbody>
</table>

**FORUM ON FUTURE RESEARCH**

• Development of a Decision Support System for Chemical Accident Information
• A Robust Sensor Fault Diagnosis System Using Neural Networks and a Dynamic Process Model
• Issues in Fault Diagnosis and Isolation
• Chemical Plant Safety Performance Measurements
• Electrostatic Hazards and Class I Flammable Liquids
<table>
<thead>
<tr>
<th>Please Print Clearly</th>
</tr>
</thead>
<tbody>
<tr>
<td>Last Name</td>
</tr>
<tr>
<td>Company Name</td>
</tr>
<tr>
<td>Mailing Address</td>
</tr>
<tr>
<td>City</td>
</tr>
<tr>
<td>Telephone</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Additional Persons Registering: ($50.00 discount per person when registering five or more from the same organization)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2) ___________________________________________________________________________</td>
</tr>
<tr>
<td>3) ___________________________________________________________________________</td>
</tr>
</tbody>
</table>

Please indicate preferred track for session attendance:

**Day 1** - First Session: Track I  Track II  Track III  Second Session: Track I  Track II  Track III  Third Session: Track I  Track II  Track III

**Day 2** - First Session: Track I  Track II  Track III  Second Session: Track I  Track II  Track III  Third Session: Forum on Future Research

**REGISTRATION FEES**  (Fee includes refreshments, lunch, handouts and Proceedings)

- Received by October 1, 2001 - $395.00 per person  •  Received after October 1, 2001 - $450.00 per person  •  Purchase of printed proceedings and CD-ROM (set) only - $65.00

☐ Payment by Check  
*(payable to Mary Kay O'Connor Process Safety Center)*

**Total Enclosed** $ __________________

☐ Payment by Credit Card

☐ MasterCard  ☐ Visa  ☐ American Express  ☐ Diners Club

**CC#** ________________________________

**Card Holder** ____________________________  **Exp.** ____________

**Total Charge** $ __________________

**Accommodations:**

When making reservations, please indicate that you are attending the Mary Kay O'Connor Process Safety Center Symposium. ROOMS WILL BE RELEASED TO THE GENERAL PUBLIC AFTER SEPTEMBER 25, 2001.

Rooms have been blocked at the following motels:

- Hilton  (979) 693-7500  Single rate: $73 (has shuttle)
- Holiday Inn Expr.  (979) 846-8700  Single rate: $69 (has shuttle)
- Manor House Inn  (979) 764-9540  Flat rate: $56 (has shuttle)
- Hampton Inn  (979) 846-0184  Single rate: $69 (has shuttle)
- La Quinta Inn  (979) 696-7777  Single rate: $69 (has shuttle)
- Quality Suites  (979) 695-9500  Flat rate: $76

**Travel:**

You can travel to College Station by flying into the Easterwood Airport in College Station from the Houston Intercontinental or the Dallas/FortWorth Airport. Also, you can drive from Houston Intercontinental, which is about an hour and a half drive.

**Parking:**  Complimentary parking is available at Reed Arena during the Symposium.

**For more information:**  Contact Donna Startz at  E-mail: donnas@tamu.edu  •  Phone: (979) 845-3489

[http://process-safety.tamu.edu](http://process-safety.tamu.edu)
Baseline Measurement of Chemical Safety

After analyzing many different databases, the Center selected five databases from which to establish the baseline measurement. The year 1998 was selected as the initial year because reasonably complete data was available for that year throughout each of the data sources.

The Center acknowledges that the existing data is not perfect. The review of the databases ultimately provided the Center with the opportunity to identify limitations in the nation’s ability to accurately report incidents and to determine the number of chemical incidents. The data, as it stands now, is not easily accessible, nor is there a common language between databases. To improve this situation and provide more accurate measurements in the future, the Center is establishing a national repository.

General Trends in Incidents, Fatalities, and Injuries

Existing data sources do provide useful information about chemicals and industries that are frequently involved in chemical releases. However, much of the incident data has not been collected with enough consistency to establish trends over a long period of time. Thus, any trend analysis relies primarily on the application of indirect indicators of chemical incidents and injuries. The following items were noted in the Center’s review of the data:

- The number of incidents occurring at fixed facilities appears to be flat;
- There appears to be a downward trend in oil spills on navigable waters,
- The number of incidents involving natural gas transmission, distribution, and hazardous liquids pipelines appears to be flat;
- An upward trend in chemical incidents involving air transport appears to be occurring;
- Fatalities, as a result of chemical incidents, show a downward trend, except for transportation-related fatalities, which appear to be flat; and
- Injuries from chemical incidents show similar trends in fixed facilities, on highways, and on rail transport; however, injuries related to pipelines and air transports seem flat.

Simple observation reveals that progress has been made in protecting people from injuries and fatalities due to chemicals over the periods of time reported in the five data sources reviewed. There seems to be no clear evidence of a reduction in the number of chemical releases as measured by data from U.S. Environmental Protection Agency (EPA).

Causes and Patterns of Incidents

In order to target critical risk management activities, the Center looked at the types of chemicals, processes, and equipment; operating modes; time of day; and other factors commonly associated with incidents. Some of the observations from the analyses are:

- There are 12 industry/chemical combinations that account for 75 percent of releases as reported under EPA’s Risk Management Program (RMP) Rule. Specific activities should be undertaken that address these areas.
- Overall, small releases have consequences (numbers of injuries) similar to large releases. This is probably due to the larger number of small releases offsetting the lower number of large releases. This fact is demonstrated by a review of two different databases that provide incident information for the relatively volatile chemicals: ammonia, chlorine, concentrated acids, and light hydrocarbons.
- Mechanical failure seems to be more likely than human error to be the initiating event in a chemical incident. This analysis is based on the review of four independent incident databases.
- Injury consequences are widely distributed across facilities of all sizes (as measured by number of employees). This appears to be contrary to the beliefs of some that most incidents occur at smaller facilities due to a perceived lack of expertise in chemical safety.
- More incidents occur during the daytime when activity is increased and when more employees
are likely to be exposed. The proportion of human error compared to mechanical failures also increases during daylight hours.

- Several databases indicate that approximately half of the reported releases are from industries that use, store and distribute chemicals, rather than chemical manufacturers and petroleum refiners.

### Public Trust and Community Interaction

In order to better understand the issues surrounding public trust and community interaction, the Center conducted a survey to measure the level of public knowledge and trust of chemical operations. The baseline survey indicates one major finding—communities have a low level of awareness of the presence of hazardous chemical facilities in their community. Between 50 percent and 67 percent of people living within a one-mile radius of an RMP-covered facility were unaware of the chemical facility. However, those that receive information about chemical facilities believe the information is helpful in protecting their families. There also is a preference to receive the information from local emergency planning committees (LEPCs) or local companies. Considering these three points, it seems clear that LEPCs, CAPs, and local companies should work together to inform the public near chemical facilities of the hazards and appropriate emergency response measures.

In addition, the survey showed that 81 percent to 88 percent of people surveyed would feel safer knowing that EPA and the U.S. Occupational Safety and Health Administration were providing accident prevention and hazard reduction to the company.

### Conclusion

This initial review does not necessarily provide specific answers for preventing incidents. However, it lays the groundwork and provides direction for further action by the Center and all stakeholders towards realizing the National Goal.

---

### RECENT PUBLICATIONS


---

For information on the 2001 Symposium, see our website at:

http://process-safety.tamu.edu

or call (979) 845-3489
Conclusions

As a matter of general practice, extreme caution should be observed in work on equipment constructed from titanium and vessels with titanium internal components. Specific conclusions and measures identified or suggested as a result of this incident and follow up activities are:

- Accumulations of iron oxide (or other materials such as organic residues, pyrophoric substances, etc.) on titanium structured packing can promote or accelerate combustion of titanium. It may be appropriate to periodically remove accumulations of such materials through chemical or other means. However, if removal is accompanied by loss of titanium, it can create thinner metal, which may be even more sensitive to ignition.

- Use of water to mitigate an active titanium metal fire can produce negative as well as positive effects.

- Measures that may be used to prevent ignition during maintenance of towers containing structured packing made from thin sheet titanium include the following:
  - Keeping the packing wet with water
  - Flooding the tower with water to a level just below the work area
  - Isolating the packing from the work area using physical barriers such as non combustible blankets
  - Strictly controlling hot work

Entry procedures for towers containing structured packing made from thin sheet titanium should account for situations where the packing is coated with combustible materials, pyrophoric substances, or materials that can react with the packing (e.g., iron oxide).

INCIDENT 2: TITANIUM FIRE IN CHEMICAL PLANT

A fire was reported inside a tower at a chemical plant. The emergency response organization responded immediately and brought the incident under control. One minor first aid injury occurred to an employee who was treated and released to return to work that afternoon. As a result of the fire, the vessel was burned through, around the entire circumference of the shell, in two places. No other equipment in the structure sustained damage.

Background

The tower is a 316 stainless vessel that is 42 inches in diameter and 73 feet tall. It contains three beds of packing. The top and middle beds were titanium, the bottom bed was Inconel. This metallurgy was changed from stainless steel during the last turnaround due to severe corrosion of the packing material. This was the first time the tower had been opened for work since that time.

On Sunday, the tower experienced an operational upset caused by a plug in the tower that prevented the downward flow of liquid. The tower was taken out of service on Sunday night. Gas freeing and mechanical preparation took place on Monday. Final preparations for vessel entry were being made on Tuesday morning when the fire occurred.

Data/Observations

- The titanium packing in the top bed had broken into small pieces and was falling through the top bed support tray. Before the fire, significant quantities of small pieces of titanium were observed on
the liquid redistribution tray above the middle packing bed.

- Unit operations first became aware of the incident when a manway was moved and a flash fire occurred. This phase of the incident was over very quickly, however, several minutes later a bright spot of glowing metal appeared on the tower that rapidly grew in size and intensity. Shortly thereafter, a second glowing spot appeared on the tower about 10 feet above the first.

- The lower tower burn-through occurred just above the mid-point of the middle packing bed. The upper tower burn-through occurred in the area of the liquid redistribution tray above the middle packing bed.

- Titanium is classified as a flammable metal. Depending on size, titanium auto-ignites at temperatures between 630 and 2050 deg-F (lower temperature for powder, higher temperature for solid). The presence of steam reduces the amount of air and/or the temperature required for auto-ignition. Once small shavings are ignited, the fire is self-sustaining.

- Analytical results and consultation with titanium manufacturing experts confirm that we experienced a Class D metal fire involving titanium inside the tower.

**Conclusions**

- A titanium fire caused the extensive damage to the tower. The presence of small particles of titanium in the middle packing bed significantly contributed to the ease of ignition of the titanium and accounts for the tower burn-through in these locations.

- The most likely mechanism for ignition is the presence of pyrophoric residue.

- The presence of metal oxides accelerated the oxidation of the titanium via a mechanism known as the Thermite Reaction in which the oxygen for combustion is taken from a less reactive metal oxide.

- The investigation was unable to determine if the Class D fire at the mid-bed point started before or after the observed flash fire at the manway.

Until more is known, extreme caution should be used when working on any vessel with titanium internals. This is especially true if damage has occurred that has resulted in the presence of small titanium particles or if other metal oxides are present that might provide a source of oxygen.

**EMERGENCY ADDITION TO FIRE PROTECTION MANUAL**

**Hot Work Inside Columns with Structured Packing**

Many columns contain internal beds made of structured packing, especially columns in which pressure drop is a significant issue. Crude atmospheric and vacuum distillation columns, FCC and coker fractionators, as well as some distillation columns in chemical plastic manufacturing may contain beds made of structured packing. Structured packing can consists of very thin gage (almost foil like) layers of metal, corrugated within a support grid, in other cases structured packing is thicker metal that is called grid. Structured packing and grid provides a very high surface area to volume ratio that difficult to clean and provides a good venue to start a fire, like stacked kindling. Structured packing is typically loaded in sections and layered like bricks in either single or multi-bed configurations.
Normal cleaning processes do not adequately clean hydrocarbon and fine coke material off of structured packing. In a test in a refinery, structured packing that was chemically cleaned, steam cleaned, removed from the column and additionally externally cleaned still contained sufficient hydrocarbon to be ignited. There have been several instances where a source of ignition (hot work), oxidation of FeS, or reactive chemicals has started small fires within the packing. New packing is often coated with a thin layer of oil that also is a fuel source. The heat from these initial fires was sufficient to ignite the metal packing resulting in a very hazardous metal fire that is difficult to extinguish.

Some specific fire protection issues associated with structured packing are:

- The metal in the packing itself is a potential source of fuel. Structured packing (and on occasion - even random packing) metal can burn and create a “metal fire”. (Remember the high school chemistry class where you saw steel wool **burn** over the top of a Bunsen Burner.) If a relatively small fire occurs in a packed bed, its heat can ignite the metal and create a much more serious, intense fire.

- When doing work over packed beds, consider the packing to be a potential fire hazard. People doing work over packed beds of any type, new or old, need to treat it as if they are working over a major fuel source. This combined with the difficulty in removing all the hydrocarbon from the packing makes it imperative to isolate the packing from the hot work with substantial plywood decking and fire blankets sealed off at the column walls. Plywood cut to the vessel radius should be placed under the fire blankets to prevent wearing a hole in the fire blankets. The seams in the plywood and the edges of the decking should be sealed using duct tape. Consideration should be given to chemically treating the plywood to make it more fire resistant. Fire blankets (cloths) must be lapped a minimum of 4 inches and the laps sealed with duct tape, including the lap to the vessel wall. A minimum of 2 blanket layers with seams orientated 90 degrees should be used to minimize the potential for welding or grinding sparks to reach the packing.

- Hot work inside columns with structured packing must always be wet work. Keep fire blankets wet while hot work is occurring above packed beds. A fire hose should be pressurized and used to extinguish any embers that are generated during any hot work (welding and grinding). Fire watches should be trained to inspect and stop the hot work if holes or tears are found in the fire blankets.

- The job planning process needs to ask the question “How can we avoid hot work over the structured packing?” The inherently safer solution is to remove the packing prior to conducting hot work. A Job Safety Analysis should be conducted to address the specific risks and mitigation prior to commencing hot work over structured packing.

- A contingency plan should be prepared and reviewed with all operators and mechanics before hot work begins. These contingency plans need to address the precautions needed to prevent/suppress a “metal fire”. These include:
  - Removal of the packing prior to doing hot work is the best approach to be sure absolutely that a fire cannot occur in a column.
  - In some cases, removing the packing is not attractive especially for small hot work jobs. In these cases, redundant sealed barriers between the packing and the hot work area, such as requiring two or more layers of fire blanket with a plywood support underneath. The blankets should be soaked with water while the hot work is being performed.

*(Titanium Safety Alert continued on page 18)*
Ability to put substantial firewater on the initial fire quickly
- Ability to quickly close up the column to stop the oxygen supply, or to quickly inert the column. This is especially true when multiple manways have been removed and scaffolding or other equipment has been installed which inhibits re-installing the manways. Consider how welding cables, electrical lines, air lines, ventilation lines, etc. can be quickly removed from the manways. Light weight metal covers should be placed near the manway openings so that one person can quickly seal the opening. Personnel should be instructed how to install and seal the openings.

- Implement initial and ongoing processes to inspect the site and verify the work is occurring safely and that the barriers are being maintained. A critical protection is a dedicated fire watch with the responsibility for monitoring the hot work and who has the authority to stop the work if they observe unusual or unsafe conditions. The fire watch should review the area after the hot work has been completed to assure that a smoldering fire has not slowly developed.

- Also, packed beds should be monitored during initial vessel entry. Pyrophoric iron sulfides or reactive chemicals can cause fires as the packing dries out, even when no hot work is occurring. The precautions listed above for extinguishing a packing fire should be followed in columns with pyrophoric iron sulfide or reactive chemical concerns.

EXHIBIT SPACES ARE STILL AVAILABLE

Booths are still available for exhibits at the 2001 Mary Kay O’Connor Process Safety Center Symposium.
Just complete the following form, then fax or mail to reserve your space today.

EXHIBIT REGISTRATION • 2001 Symposium
Mary Kay O’Connor Process Safety Center
BEYOND REGULATORY COMPLIANCE, MAKING SAFETY SECOND NATURE
October 30-31, 2001 • Reed Arena • Texas A&M University • College Station, Texas

Please Print Clearly

<table>
<thead>
<tr>
<th>Company Name</th>
<th>Contact Name</th>
<th>Mailing Address</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>City</th>
<th>State</th>
<th>Zip</th>
<th>Email Address</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Telephone</th>
<th>Fax</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$1250 fee includes: One 10 X 10 booth, electrical hookup, ethernet line, table, curtain backdrop, and one symposium registration.

☐ Payment by Credit Card
To: Phone: (979) 845-3489
Fax: (979) 458-1493
Email: donnas@tamu.edu
☑ MasterCard ☐ Visa ☐ American Express ☐ Discover

CC# ____________________________
Exp. Date _______________ Total $________

☐ Payment by Check
Total Enclosed $__________________
Please send registration form and check (made payable to Mary Kay O’Connor Process Safety Center) to:
Texas A&M University
Mary Kay O’Connor Process Safety Center
Attention: Donna Startz
3122 TAMU
College Station, TX 77843-3574

For more information, contact Donna at: Mary Kay O’Connor Process Safety Center, Texas A&M University, 3122TAMU, College Station, TX 77843-3122
Ph: (979)845-3489 • Fax: (979)458-1493 • E-mail: donnas@tamu.edu • URL: http://process-safety.tamu.edu
2001 Calendar

Monday, Oct. 29, 2001
MKOPSC Executive Forum Meeting
10 AM - 5 PM
Texas A&M University • CE/TTI Office Tower, Room 217C

October 30 - 31, 2001
MKOPSC Symposium
Reed Arena • Texas A&M University

Thursday, November 1, 2001
MKOPSC Technical Advisory Committee Meeting
9 AM - 5 PM
Texas A&M University • Zachry Engineering Center, Room 342