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Chemical Safety: Asking the Right Questions

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Introduction

Recent reports have shown that, despite efforts to the contrary, chemical accidents continue to occur at an unacceptable rate and there is no evidence that this rate is decreasing. Based on this observation, one can conclude that previous analyses have not accurately identified and implemented appropriate fixes to eliminate identified root causes for chemical events. Based on this, it is time to reevaluate chemical accident data with a fresh eye and determine a) what corrective actions have already been identified but have not been implemented, b) what other root causes may be involved, and c) what new corrective actions should be taken to eliminate these newly identified root causes.

Chemical Accident Analyses

In the last five years, two reports analyzing the causes of chemical accidents have been published. One report, published by the U.S. Chemical Safety and Hazard Investigation Board (CSB) titled "*Hazard Investigating: Improving Reactive Hazard Management*," [1], analyzed 167 accidents that had occurred over a 22 year period in the United States. Accidents investigated in this report were those that resulted in loss of life, and/or significant loss of property coupled with significant environmental damage. The other, published by the Department of Energy titled "*Recommendations for Addressing Recurring Chemical Incidents at the U.S. Department of Energy*" [2], analyzed 390 chemical accidents that occurred at DOE facilities between 1998 and 2002. While a few accidents evaluated in this report were of a significant size, most were on a much smaller scale than those investigated by the CSB.

Accident Similarities

Of major significance is that both of these reports made similar observations as to accident causes and similar recommendations as to how these root causes could be mitigated. The reason this observation is significant is that it shows that chemical events may stem from the same issues regardless of the event size. In other words, issues that can lead to small events are essentially the same issues that can lead to large events. This observation leads one to logically conclude that a significant root cause is fundamental to all chemical work. The obvious and essential question that arises from this conclusion is "What is this root cause?"

Information from Previous Chemical Accidents

One area of investigation in both the CSB and DOE studies focused on analysis of the types of chemical hazards involved in these incidents. Chemical hazards included acids, bases, other corrosives, flammable and combustible liquids, oxidizers, water-reactives, shock-sensitive compounds, pyrophorics, explosives, compressed gasses, asphyxiants, toxics, and generally unstable chemicals. What was observed was that chemicals involved in the majority of these incidents were not limited to a single hazard class or even to a few classes (It should be noted that most chemicals involved in these incidents had more than one class of hazard.) Both the CSB and DOE studies observed no clustering of incidents involving acids, oxidizers, monomers, water-reactives, bases, alcohols, organic peroxides, inorganics/metals, or any other chemical class.

Since no clustering of chemical classes was observed in these incidents, the possibility that some other common factor being involved was investigated. Chemicals regulated by the Occupational Safety and Health Administration (OSHA) and the Environmental Protection Agency (EPA) were then evaluated as significant causes of chemical accidents. OSHA's regulation, *Process Safety Management of Highly Hazardous Chemicals* (29 CFR 1910.119) (PSM), covers approximately 130 chemicals that have the potential for causing or being involved in chemical incidents. Likewise, EPA's regulation, *Chemical Accident Prevention Provisions* (40 CFR 68) (RMP), lists approximately 70 chemicals that are to be evaluated. Of the 390 chemical incidents that were analyzed in the DOE report, only 30 involved regulated chemicals on either of these lists. Similarly, the CSB stated that less than 40% of the chemical incidents they investigated involved regulated chemicals. Once again, the absence of incident clustering based upon this selection criterion was noted.

The hazard rating system described in NFPA 704 was then examined with respect to the incidents reported. An effort was made to determine if chemicals involved in these incidents had a high instability (formerly reactivity) hazard rating according to NFPA 704 criteria. Of the 390 chemical incidents evaluated in the DOE report, ratings were published for only 145 of those chemicals involved in the accident and, of those, 47 had hazard ratings of "0" or "1," indicating low hazard. This means that 75% of the incidents involved chemicals with either no instability rating or a rating of "0" or "1." These results form DOE mirrored those of the CSB, which reported that chemicals with high instability ratings were not always involved in chemical incidents. The CSB found that almost 70% of the chemicals involved in the incidents they investigated were either unrated or had an instability rating of “0” or “1.” This would indicate that NFPA hazard ratings have a limited potential as a screening tool to predict chemical incident scenarios.

The next line of inquiry involved the type of work being performed during the incident. Both the DOE and the CSB reports indicate that the type of work being performed during the chemical event was not a factor. Work involving chemicals that resulted in incidents included laboratory experimentation, storage, process operations, transportation, etc. Equipment used in each incident also varied widely, eliminating another possible factor. The same was true of incident types. Incident types varied (e.g., spills, fires, explosions, exposures), and no one type of incident occurred at a significantly greater rate.

Lastly, rates of chemical accidents do not appear to be decreasing. The DOE report indicated that accident rates were either flat or increasing. While the CSB report did not evaluate whether or not the frequency of accidents was increasing or decreasing, the frequency of news reports concerning chemical accidents does not provide the appearance that the rate of chemical accidents is not significantly declining.

These analyses indicate that few, if any, chemical incidents are similar. The various incidents involve different chemicals, at different concentrations, in different environments, in different uses, and with different pieces of equipment. This means that no simple fix can be engineered to address specific chemicals, processes, equipment, or environments. Being that there appears to be no clustering of accidents based upon scale of operations, chemical type, hazard rating, work being performed, or equipment being used, it would appear that the overall root cause may simply be that the difficult and complex nature of chemistry makes the identification of a potential chemical accident difficult and if one is unable to identify potential chemical accidents, then one is unable to mitigate the hazard no matter how good or efficient existing systems are.

Failure to Identify the Hazards

The CSB analysis of 167 incidents over a 22-year period showed that over 60% of such incidents had as one of the root causes "inadequate hazard recognition and evaluation", with the emphasis on identification (Figure 1). Similarly, the DOE report stated that "failure to identify the hazard" was a primary cause in the majority of the accidents evaluated. If this is a significant root cause for many chemical events, then one must determine the reasons why it is so difficult to determine chemical hazards.

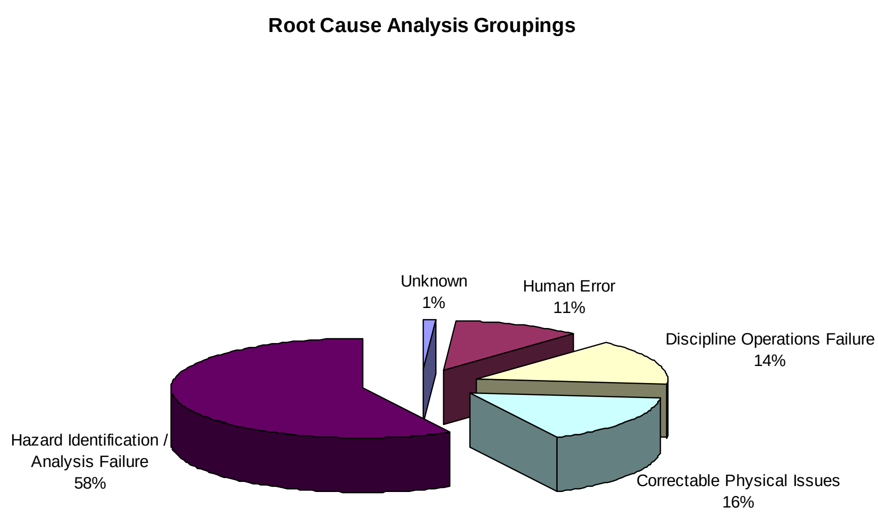

Figure 1 Analysis of CSB and DOE Data

Difficulties in Chemical Hazard Determination

A significant factor contributing to the complexity of chemical hazard identification is the multitude of chemical regulations that various federal agencies have promulgated (e.g., DOE, EPA, OSHA, and the Department of Transportation (DOT)) as well as various consensus standards that the government and/or industry has incorporated (e.g., National Fire Protection Association [NFPA], Compressed Gas Association [CGA] and local fire codes). DOE recently published a partial listing of chemical safety regulations from Federal sources [3]. This listing did not include requirements for waste, off-site transportation, or local regulations and still contained approximately 1,500 requirements from more than 130 sources and represents an extraordinary number of regulations to be understood and implemented.

Another factor making chemical hazard identification difficult is the organization of chemical regulations. These regulations are usually promulgated by chemical type (e.g., NFPA 30, Flammable and Combustible Liquids Code; NFPA 430, Storage of Solid and Liquid Oxidizers; 29CFR1919.101, Compressed Gases) which is not how work is many times performed. What makes this even more difficult is that different organizations are usually responsible for different blocks of requirements. For example, a company's fire protection group may be responsible for NFPA codes, their safety organization may be responsible for compressed gas requirements, and the company's industrial hygiene group may be responsible for hazard communication and other related standards. This natural organization outcome of the requirements' organization can easily result in "stovepiping". When "stovepiping" occurs, there is the risk that various organizations do not communicate as well as they should and that employees will "answer shop" until they get the answer they want. All of this can conspire to make chemical hazard identification more difficult than necessary.

Another issue making chemical hazard identification more difficult is the complex nature of chemistry. There are an enormous number of chemicals known and their ability to react with other chemicals in the process or in their surroundings is even greater. There are more than 12 million (and counting) known chemicals. Each of these chemicals can undergo a variety of reactions. Moreover, not all reactions are well known or documented, even for well-researched and/or widely-used chemicals. Additionally, these reactions are dependent on concentration, temperature, physical form (e.g., fine powder vs. granular), state (e.g., gas vs. liquid vs. solid), presence of contaminants that may catalyze or inhibit reactions, etc. Variability of temperature, coreactants, concentration, contaminants, etc., is too complex to be captured in a document as simple as a Material Safety Data Sheet (MSDS) or any other single reference.

Lastly, chemical hazard identification is difficult when one factors in chemicals with multiple hazardous properties (e.g., an oxidizing acid or a combustible acid), when reaction scale changes, when concentrations change, etc. For such situations, it is sometimes difficult to reconcile conflicting process and regulatory requirements or determine if new hazards are present or old hazards eliminated. Examples include:

- If an acid is controlled by rules regulating corrosives and you want to dilute the acid, then at what point is the acid no longer considered a corrosive that is governed by those rules?

- When NFPA codes require a water-based fire suppression system for flammable liquids, then how do you store a flammable liquid that also happens to be a water-reactive material?
- What regulations take precedence for a highly toxic, flammable gas – those for highly toxic gases or those for flammable gases?
- Do heat transfer techniques that worked for a 30 gallon reactor still work when scaled up to a 500 gallon reactor?

Questions such as these are routinely encountered, and often no easy answer is available.

Today's State-of-the-Art

Numerous attempts have been made to develop systems that will result in safer chemical usage; however, none have been as successful as developers had hoped. Some of these systems are developed around hazard types, but as shown above, some chemicals do not fit neatly into hazard categories.

One approach is based on the Process Safety Management (PSM) regulation. PSM contains a list of approximately 130 chemicals that are used in industry. This regulation stipulates that, if any chemical on the list is present in quantities greater than or equal to the thresholds listed, then various actions must be taken to insure safe operation of the process using the chemical. This type of system has its own weaknesses. First, the list is not all-inclusive. Many more chemicals than the 130 on the list are used routinely. If a chemical is not on the list, or is on the list but in quantities below the regulatory threshold, then the process does not require analysis under the regulation. That does not mean that a significant hazard is not present. Another weakness with this type of system is that it tends to provide a false sense of security. If no listed chemical is involved in the work to be performed, one tends to feel safe in that there are no significant chemical hazards to consider.

Another approach uses specific hazard ratings to identify potential chemical hazards. One weakness of using ratings to screen for hazards is that not all chemicals have been rated. If the chemical in question has not been rated, the system cannot be used for analysis. Also, chemical hazard ratings are based on hazards present in a given standard set of conditions that may or may not represent the existing conditions for the process being evaluated. If conditions for the process are different than those used to develop the ratings, the published ratings may provide an inaccurate picture of incident potential. Lastly, focusing on specific chemical hazard ratings can cause other issues to be ignored. The CSB reported that too narrowly focusing on toxicity hazards resulted in an incident because other chemical hazards present were not evaluated [4].

A third approach assigns various aspects of chemical safety to different organizations/ disciplines (i.e., “stovepiping”). A typical approach assumes that the industrial hygienist should be responsible for IH issues such as personal protective equipment (PPE) and monitoring, that a fire protection professional should be responsible for issues such as NFPA regulations (e.g., the “NFPA Diamond” from NFPA 704), etc. This leads to a fragmented program that typically has many holes in the coverage and will be inconsistent from organization to organization.

One aspect in common with all of these approaches is that chemical safety is typically assigned to traditional disciplines such as industrial hygiene or chemical engineering. If chemical safety is to be the responsibility of industrial hygiene, chemical engineering, or any other individual technical discipline, then the personnel involved should have sufficient qualifications and/or experience, which are generally beyond the scope of traditional education and training of these disciplines, to identify and analyze the hazards.

Recommendations

Previous solutions have not been, nor will they every be, successful. Other approaches must be devised. These approaches must avoid "stovepiping," must ensure that people with the necessary education and experience are involved, and must promote a clear understanding of codes and regulations and their intents.

Recognition of Chemical Safety as a Unique Discipline

Chemical Safety is not an easy area to understand given the large number of regulations and its technical aspects, as is the case for other safety disciplines (e.g., fire protection, industrial safety, and industrial hygiene). Furthermore, a genuine understanding of Chemical Safety requires a knowledge base well beyond that of the traditional safety professionals. If the overall cause for these chemical incidents is a failure to identify the hazards, then management needs to improve the core function of "Identify and Analyze the Hazard" and "Develop and Implement Hazard Controls

This can only be accomplished if managers recognize that Chemical Safety is a separate and unique discipline. They need to accept the fact that it is not an easy area to understand, and they must ensure that they have the resources to cope with its complex technical aspects. Managers also need access to individuals who have critical chemical knowledge, including an understanding of chemical thermodynamics, reactivity hazards, chemical process hazards, and explosion hazards. Laboratory or chemical process knowledge and experience are also crucial, because they provide hands-on knowledge of chemical behavior, limitations of laboratory or chemical process equipment, and potential alternatives that would make the work safe. Knowledge of hazardous materials response would also be useful.

A chemical safety professional should understand certain critical concepts such as chemical thermodynamics, redox reactions, reactivity as a function of surface area, the Carnot cycle (including concepts such as adiabatic compression), and reaction energies (e.g., Gibbs free energy, heats of combustion, entropy). These and other important concepts are not covered in detail until advanced chemistry courses.

Chemical safety professionals should also have laboratory or other hands-on experience because:

- They receive hands-on knowledge about what chemicals can and given the opportunity will do.
- They learn how various pieces of laboratory or industrial equipment (including analytical instrumentation) work and what their limitations are.
- They are familiar with various standard laboratory or production activities, which will assist in the design of methods to mitigate chemical hazards while minimizing the impact on the work being performed.

Chemical safety professionals should have training or experience in hazardous materials response. This would provide them with practical information about the recognition, prevention, and mitigation of the potential of chemical incidents.

Ownership

Management needs to establish ownership for Chemical Safety, so that people will know where to go for authoritative chemical safety answers. The owners of Chemical Safety have a responsibility to ensure that the correct analysis was performed and the best answer was given. Having responsibility over a defined area of safety forces one to take ownership of analyses that are performed and answers that are given in order to determine if an activity can be performed safely. This, in turn, forces the owner to ensure that those involved in the analyses and decision-making are qualified.

Conclusion

In this manuscript we have shown chemical related incidents occur at an alarming rate in spite of our best efforts to identify and mitigate potential hazards. The analysis of these events suggests that the implementation of Chemical Safety, vies-a-vie hazard identification, in both industry and government facilities is woefully inadequate. To remedy the situation we propose that Academia, Industry, and Government join together and establish training and experience requirements so that the personnel performing in this capacity can become qualified as Chemical Safety Professionals.

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