Challenges of Regulating or Implementing Reactive Chemicals Hazard Management Program

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This statement was prepared by the Mary Kay O'Connor Process Safety Center (MKOPSC) at Texas A&M University. Founded in 1995, the Center conducts programs and research activities that enhance safety in the chemical process industries. The Center's educational activities promote safety as second nature to everyone in the industry. In addition, the Center develops safer processes, equipment, procedures, and management strategies to minimize losses within the processing industry. The Center supports the US Chemical Safety and Hazard Investigation Board (CSB) and welcomes opportunities to assist the CSB in its mission to improve safety in the process industry.

Reactivity is the ability, or propensity under certain conditions, of a pure chemical or a mixture of chemicals to undergo chemical change or combine with other chemicals. The nature of some chemicals to be highly reactive can be very beneficial, and this reactivity makes possible a wide variety of synthesized products and a high standard of technology. However, uncontrolled reactivity or lack of knowledge about reactions has led to numerous incidents.

While it is generally accepted that reactive chemical incidents pose a significant safety problem, there is very little agreement on how to regulate or implement a reactive hazard management program. The CSB in its recent study identified 167 reactive chemical incidents since 1980 that caused 108 deaths to workers and the public. More than half of the incidents involved chemicals that are not explicitly covered by the PSM standard or the RMP rule.

The CSB stated in its study that industry is not utilizing the available chemical reactivity information sufficiently. According to the CSB, "In at least 90% of the 167 incidents, information on the hazards was obtainable from publicly available literature. However, federal work place safety regulations contain few specifics on the need to review reactive hazard information." The CSB also found that there is no single repository of information on runaway chemical reactions making it difficult for industry and government agencies to identify patterns that might promote safer handling.

To summarize, reactive chemicals represent a significant hazard and have contributed to a large number of incidents resulting in fatalities, injuries, and property losses. However, the CSB study and other information available in the open literature leads us to conclude that a majority of the reactive chemical incidents occurred because the owner/operator of the facility did not make use of the information easily available in the literature. In a smaller fraction of the incidents, the owner/operator did not have complete knowledge of the process chemistry involved.

Many materials whose NFPA instability ratings are equal to 1 or 2 were involved in these incidents. For example, Napp Technologies in Lodi, NJ, involved the reaction of aluminum powder (NFPA Instability rating = 1) and sodium bisulfite (NFPA Instability rating = 2), which resulted in tragic worker injury and death as well as extensive damage to the immediate surroundings. The specific incident at Napp Technologies was the direct result of the *inter-reactivity* of two materials (aluminum and sodium bisulfite, mediated by water), which released significant amounts of energy. Many (if not the majority) of reactive chemicals incidents fall into this category of *incompatible inter-reactivity*. The chemical industry has spent considerable effort to understand chemical inter-reactivity and its role in assessment of potential hazards[1,2]. Understanding inter-reactivity involves quantification of the kinetics and thermodynamics of the interaction of two (or more) materials and the impact of that energy release on the immediate surroundings. The instability rating, a measure of a material's thermal stability, generally at ambient conditions, cannot be used to predict a material's inter-reactivity with other materials.

For similar reasons, a list-based approach to regulate or implement a reactive hazard management program will not work. There are approximately 18,000 chemicals in industrial use and an endless combination of chemicals, surfaces, and contaminants. The complexity of understanding the unstable behavior of any one of these chemicals can be quite daunting.

Another highly publicized incident is the Concept Sciences incident involving runaway reaction of hydroxylamine. While knowledge regarding the potential for unstable behavior of hydroxylamine goes as far back as a paper published in ***Science*** in 1899[3], detailed process chemistry information as well as the catalytic effects of various metals and their oxides and elevated temperatures were not available in the open literature. Following the Concept Sciences explosion, another incident involving hydroxylamine occurred in Nissin Chemical in Japan. Following these two incidents, extensive research on hydroxylamine has been conducted at the MKOPSC as well as the National Research Institute of Fire and Disaster in Japan. This research has led to an increased understanding of the behavior of hydroxylamine reflected in several publications[4,5,6,7] and a PhD dissertation[8]. However, the research conducted so far has allowed us to barely scratch the surface with regard to understanding of the unstable behavior of hydroxylamine. Even as we speak, further work continues to understand the unstable behavior of hydroxylamine under industrial conditions[9,10,11,12,13].

What is the path forward?

The appropriate and safe production, handling, and storage of chemicals is a complex issue requiring deep knowledge of the potential energy of the materials, how that energy can be released (lack of intrinsic stability or inter-reactivity with other materials) and its potential impact on the immediate environment. Regulation by intrinsic reactivity alone or a list-based approach will not impact situations where materials inadvertently mix and react, or the control of an intended reaction between two (or more) materials is lost and the rate of energy release exceeds the ability of its surroundings to contain it. It is only through the careful assessment of the potential for energy release (under both intrinsic and inter-reactivity scenarios) and the understanding of the impact of the resulting potential energy release on the immediate environment that chemicals can be handled in a safe and environmentally friendly manner. Regulation via a simple list, in many cases, will fall short of avoiding potentially hazardous scenarios and, in some cases, may provide a fall sense of security and thus increase the risk. Our recommendations include the following:

1. Development of a publicly available and widely disseminated database on reactive chemical incidents. Efforts should be made to include root causes and lessons learned for each of the incidents in the database. In this respect, we urge the CSB to make the database of 167 incidents compiled for the recent CSB hazard investigation publicly available as soon as possible. In addition, every effort should be made to update the database on a regular and continuous basis.

2. Develop a reactive chemical information database. This database could contain information on the parameters of interest with regard to known reactivity of chemicals. As new information becomes available, the database should be updated and revised to include new chemicals or additional information about existing chemicals in the database. In order to increase the available amount of reliable reactivity information data, increased funding of research into the nature of reactive chemicals both experimental and theoretical should be pursued.

3. A recommendation should be made to every federal or state agency that as part of any reactive chemical incident investigation, every effort should be made to negotiate the public release of a summary of the incident, root causes, and lessons learned.

4. For PSM- or RMP-regulated facilities, reactive chemical incidents can be regulated or enforced based on existing regulations. For example, the process safety information paragraph of the PSM standard requires that sufficient information from reliable sources be used to identify and understand the hazards posed by processes involving hazardous chemicals. This information includes reactivity data, thermal and **chemical stability** data, and **inadvertent mixing of different materials**, **safe upper and lower limits for process variables**, and an evaluation of the **consequences of deviations**. As stated in Appendix B of the PSM standard, the chemical information to be complied must be comprehensive enough for an accurate assessment of the fire and explosion characteristics, **reactivity hazards**, and the safety and health hazards to workers.

5. For reactive chemical incidents where information is obtainable from open literature, the General Duty Clause can and should be enforced. The General Duty Clause contained in the Clean Air Act Amendments of 1990 states, "The owners and operators of stationary sources producing, handling, or storing a chemical have a general duty to **identify hazards** that may result from releases using appropriate hazard assessment techniques, to **design and maintain a safe facility** taking such steps as are necessary to **prevent releases**, and to **minimize the consequence of releases** that do occur."

6. Strategies should be developed for sharing reactive chemical data from companies who may be willing to share the data provided that the company providing the data is protected with regard to trade secrets and liability.

7. Federal and state agencies including CSB may want to issue guidance for a systematic approach to reactive hazard management. A special effort should be made to inform small and medium enterprises or enterprises with limited technical expertise in the field of the potential hazards of reactive chemicals and how to evaluate these hazards. The systematic approach should be based on a tiered framework consisting of several levels of assessment. In each level, the reactive system is evaluated to understand the reaction chemistry, identify the possibility of thermal exothermal activity, and quantify the reactive chemical hazards. Each succeeding level represents a higher degree of effort and resources. It is reasonable to suppose that a majority of chemicals or process conditions can be eliminated as representing a reactive hazard in the first level. Similarly, the second level would eliminate another set of chemicals and process conditions. Only very few chemicals or process conditions would thus require the detail or increased effort needed for the final level. As an example, consider the following three evaluation levels:

   i. screening evaluation

   ii. computation evaluation

   iii. experimental analysis

   In the screening evaluation level, reactants, products, and operating conditions are identified. Literature and databases are searched for relevant data for the various substances in the chemical system. Relevant data include physical and chemical properties, thermodynamics, kinetics, incidents, and case studies. In addition, in this level, some computations and measurements are made for a preliminary reactivity evaluation. In this evaluation level, some chemicals or reactions that clearly present no hazardous potential can be excluded from further evaluation.

   In the second level, all possible reaction pathways are proposed and their feasibility is evaluated based on available information or on predicted properties using numerical techniques such as computational quantum chemistry, statistical thermodynamics, and transition state theory. The non-feasible and non-hazardous reaction pathways are excluded and the remaining ones are tested in the third level of evaluation.

   The third level includes experimental analysis. At this level, the numbers of reactions and chemicals to be tested are reduced. More screening tests are performed to exclude more reaction possibilities and to direct the most hazardous reactions to the more advanced experimental techniques. In each of the three evaluation levels, predicting or calculating stoichiometric, thermodynamic, and kinetic parameters are the main objectives and many reaction pathways are thereby excluded from the need for expensive experimental analysis.

   More detail on this example systematic method is provided elsewhere[14]. Another method of screening reactive chemicals that takes into account both the reaction energies and the kinetics is currently under development[15]. The reason we believe that a method such as the example described here should be issued as guidance is because it will provide opportunities for better and more applicable methods to be developed.

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