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The Essential Elements of a Successful Reactive Chemicals Program

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The purpose of a Reactive Chemicals Program is to prevent uncontrolled chemical reactions that have the potential to result in injury, property damage, or environmental harm. Key to realizing this prevention is the management of the inherent energy contained in the chemicals used to produce useful products in the chemical industry. Since most chemical processes proceed “downhill” thermodynamically, it is critical to the success of a chemical process to manage that energy release in a controlled manner to prevent, for example, problematic runaway reactions. These undesired events can have extremely negative consequences in terms of injury to workers, release to the environment, and severe economic impact on the company. The Reactive Chemicals Program at The Dow Chemical Company has been in place for nearly 50 years and has evolved into a recognized industry model. This paper will discuss the various aspects or elements of this successful program and how it is implemented at scales starting in the small R&D environment and eventually to the large full scale chemical plant. Important elements include: the design of inherently safe systems, personal ownership of the reactive chemicals issues, and commitment to fully understanding of the energy release hazards of the process, including how to mitigate them.

Also discussed is the experimental testing program employed to help define the so-called “safe operating envelope” of the process. These tests include several calorimetric methods such as Differential Scanning Calorimetry (DSC) and Accelerating Rate Calorimetry (ARC). In conjunction with the calorimetric testing, the flammability and dust explosion potential of the processes are also studied. In addition various estimation and calculational strategies are employed as needed.

Finally the Reactive Chemicals Program culminates with mandatory Process Hazard Reviews where experts in many areas (Process Engineers, Chemists, Testing experts, Environmental experts, Operators, etc.) meet to go over all aspects of the process, ensuring every unit operation is covered and in sufficient detail to assure that the process will operate within safe boundaries. These reviews are held long before the process is started, and also periodically after the process is in operation. If changes to the process are needed, the facility must get that change evaluated for its reactive chemical implications. This is done through a formal “Management of Change” (MOC) process where experts are required to “sign off” before the change is allowed to be implemented.

1. Introduction

The purpose of a Reactive Chemicals Program is to prevent uncontrolled chemical reactions that have the potential to result in injury, property damage, or environmental harm. The word “uncontrolled” is

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underlined here to emphasize the fact that most chemical processes naturally occur with the release of heat and it is through the careful management of that heat release under controlled conditions that allow a safe operation of a chemical process. Many companies, including Dow since 1967, have developed a formalized and documented Reactive Chemicals Program to guide its employees to the effective management of these energy release hazards. The details of Dow's program are publically available through CCPS (CCPS, 2008). This paper is a brief summary of the elements and concepts of a successful Reactive Chemicals Program.

2. The Key Principles

At a high level, a Reactive Chemicals Program need not be very complex and may be distilled down to three key principles. These are:

1. Understanding of the inherent energy of our systems and conditions under which it can be released.
2. Avoiding circumstances that put people, environment, equipment or a business in potential danger.
3. Embracing the concept of "Owner Responsibility."

The first principle involves understanding the thermodynamics and kinetics of a chemical process. This is discussed in more detail below. This also relates to the concept of developing credible worst case scenarios such as runaway reactions and appropriate lines of defense (also called layers of protection) to prevent them.

The second key principle is easy to understand and mostly self evident. This relates to the inherently safe design of a chemical process including both equipment and chemistry. For example, choosing a synthetic route to the final product that involves more hazardous intermediates (nitro containing species for example) should, when at all possible, be avoided. It also implies that employees should always strive to follow existing procedures, not take shortcuts, and constantly strive to ensure the safe operation of processes they are responsible for.

The third principle is the so-called "keystone" of the Reactive Chemicals Program. After all the testing, consultation, and reviews, the owner of the project, process, or facility must make the appropriate decisions concerning reactive chemical issues. This principle ensures that the key process safety decisions are not "handed off" or otherwise transferred to someone else or another group within the organization. Ownership ensures key partnerships are developed with the process owner and other process safety experts. Owner's responsibilities include:

- Ensuring that the reactive chemical risks are identified
- Ensuring that all appropriate operations personnel have a fundamental understanding of the reactivity of the chemicals and the safe operating envelope (see below)
- Investigating and reporting all reactive chemical incidents (both "Learning Experiences" and Reactive Chemicals Accidents)
- Including reactive chemicals information in the operating discipline and training
- Evaluating changes for reactive chemicals potential and following a formal "Management of Change" process
- Conducting process hazard reviews for facilities on a frequent basis and for new projects
- Responding to process hazard review recommendations in a timely fashion

3. The Safe Operating Envelope Concept

Related to the second key principle above is the determination of the safe operating envelope. This concept is illustrated in a simple schematic shown in Fig. 1 below. In Fig. 1, the smaller, inner circle represents, in two dimensions, all of the parameters controlling a complex chemical process (temperature, pressure, stirring rate, cooling capacity, rate of heat release, etc.). The diameter of the inner circle is intended to represent the normal operating conditions of the process, designed to optimize the process for quality, production rate, and safety. The outer circle represents the limits of conditions during a process upset such that outside this boundary, problematic consequences will be

realized (injury to workers, equipment damage, environmental releases, for example). This is the so-called safe operating envelope and it is critical for this boundary to be well defined and understood.
The two parabolas in Figure 1 coming out from the inner circle represent two undesired process upset events. The smaller process upset takes the process outside of the normal process conditions but still well within the safe operating envelope. So while the quality of the product may be affected by this event, no process safety events will have occurred and the process will be quickly returned to the normal conditions. The consequences of larger process upset are shown to be very close to, but not beyond the safe operating envelope. So whereas this larger event may have larger negative effects on the process, the overall negative consequences are still manageable, resulting in no or minimal effect on people, equipment, or the environment.

4. Understanding the Energy Release Potential

All chemical processes proceed with energy exchange; primarily in the form of exothermic heat release. In certain high temperature cracking type operations, where entropy dominates, reactions may absorb heat in an endothermic process. It is critically important to the successful scale-up and operation of any chemical process to properly manage the expected heat release. In order to perform that management properly, several factors need to be known. First is an understanding of the heat of desired reaction but also any side chemistries which may dominate at a process upset condition. These heats provide an estimate of the worst case scenario assuming all the heat is released quickly and the contents heat up adiabatically to some temperature potentially well above the desired process temperature. If this final temperature is of concern due to secondary gassy decomposition of the reaction mix or simple vapor pressure of the reaction solvent, then engineering practices need to ensure this situation can be prevented. The common industry term for these prevention measures are “lines of defense” or “layers of protection”.

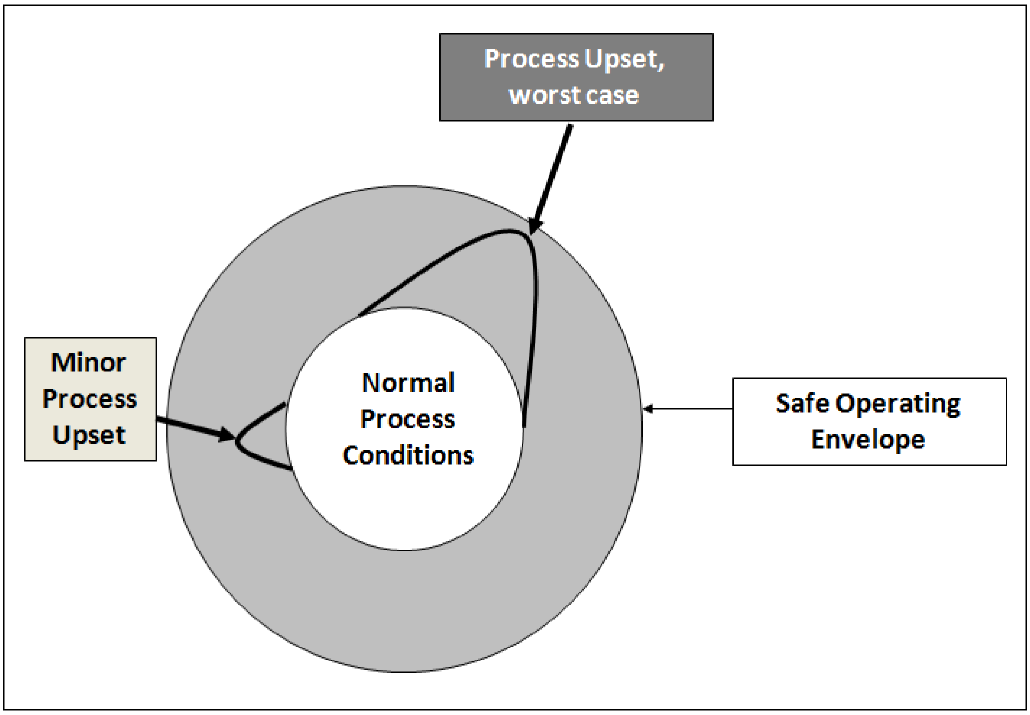

Figure 1. A simple diagram illustrating the concept of the safe operating envelope

Of course straightforward thermodynamic arguments are conservative but ignore the other main part of the energy release picture, the chemical kinetics. The kinetics (rate) of a chemical reaction dictate how fast the energy may be released in a process, slower processes are typically more inherently safe than faster processes. The reasons are fairly obvious since heat transfer to the surrounding or cooling jacket dictate whether or not a chemical process can maintain the desired temperature. In cases where the rate of heat release exceeds the heat removal rate, the temperature will increase and lead to a so-called runaway reaction which in certain circumstances, may lead to catastrophic results.

An example of the thermodynamic and kinetic aspects is a simple iron pipe lying on the ground outside in the elements. What happens is, of course, that the pipe begins to rust. The chemistry of rust formation is actually quite hot oxidation over -400 kJ per mol of iron!

$$2Fe\ (s) + 3/2\ O_2\ (g) + Fe_2O_3\ (s) \qquad (1)$$

Why doesn't this cause any hazard? It's because the process is slow enough to allow the heat release to dissipate to the environment much faster than the heat is liberated. However, if the iron is finely divided enough, it can be pyrophoric. A moderated example is commercial pocket hand warmers that may be used during outdoor activities – the reaction associated with them is faster than a rusting pipe, but certainly not as hot and as fast as a combustion reaction.

So the successful management of energy release from a chemical process involves a complete understanding of the amount of energy release (thermodynamics) and the rate of that energy release (kinetics), both under normal process conditions and conditions of a process upset.

5. The Reactive Chemicals Testing Program

Another important aspect of a reactive chemicals protocol is the experimental testing program (Frurip, 2008). Appropriately designed testing (including calculations and estimations) allows an optimum definition of process hazards and more importantly the accurate definition of the safe operating envelope boundaries.

At many companies, a risk based approach is successfully applied to the testing strategy decision process. This approach balances the scale of operations (e.g. a one liter reactor in a R&D lab versus a 10,000 L reactor in a plant) with the overall energy release potential. As an example, consider the mixing/blending of brine (salt water) with a non-volatile, high flash point polyglycol at ambient conditions at a large scale, say 5000 L. This process may not require any testing due to the known properties and known non-reactivity of these materials. Despite the fact that this is at a large scale and may have never been practiced in the plant before, the risk of not performing any testing is low enough to be deemed acceptable. On the other hand, a five liter glassware, R&D synthesis on a new substituted nitro-aromatic would probably require testing due to known energy release potential of the nitro moiety and the unacceptable risk (of injury/fatality) if the new process leads to a catastrophic energy release event.

The typical testing strategy applied is to screen first, then apply more sophisticated testing if necessary. The term "screen" means to apply less expensive, quicker turnaround, smaller scale, and less experimentally complicated tests. In the thermal stability area, Differential Scanning Calorimetry (DSC) is a commonly used screening technique (Frurip and Elwell, 2007). By "more sophisticated" testing, the application of more expensive, slower turnaround, larger scale, and more experimentally complicated tests is inferred. In the thermal stability area, this might be an Accelerating Rate Calorimetry (ARC) test (Frurip et al., 2004). Generally the more complicated tests provide more quantitative and more accurate information and are needed if the screening tests are unable to define the safe operating envelope adequately.

This strategy allows us to be efficient and economically optimized in this important area of process design. Over-testing (i.e. performing unneeded tests) can add significantly to the cost of scale up and commercialization and may be totally unnecessary. Thus by testing as needed for the scale up process, we can avoid unnecessary costs and scheduling delays.

6. Process Hazard Reviews

Process hazard reviews play an important role in any successful Reactive Chemicals Program. In Dow terminology these are called RC/PHA Reviews for Reactive Chemicals/Process Hazard Analysis reviews. These reviews are required for any new project, periodically for all facilities, and also for any new facility leader within 90 days of assuming this role. These reviews are formal meetings of several hours/days in length and follow a structured formal and globally consistent agenda. They are performed in complete partnership with the process owner (and their team). The meeting participants are part of a standing external (to the facility) committee of experts, allowing many external “sets of eyes” with broad and varied expertise to contribute to the hazard identification process. It is important to ensure that the review team is multifunctional (chemists and engineers with a wide variety of expertise) so that nothing significant is missed. It is also key to ensure that these reviews are timely (not held after the process has begun!). Finally it is important that any recommendations that result from the review are addressed in a timely manner. This can be accomplished by a joint agreement in a prioritization of the items based on defined risk. The new leader reviews, previously mentioned, ensure that the new leader is fully aware of the significant process hazards and the key lines of defense to prevent them from occurring.

Also part of the review preparation process is a detailed checklist or questionnaire consisting of many individual questions under approximately 25 categories including for example waste handling, flammability, distillation, inherently safe design, etc. This checklist is completed by the facility personnel well ahead of the review and in consultation with process safety experts and others. The level of detail here helps ensure that all relevant topics are discussed at the review to the extent they do or do not apply.

7. Management of Change (MOC)

Even a small change can cause a major reactive chemicals hazard potential. For example, these hazards can be the result of changing to new suppliers of raw materials, equipment changes, changes in procedures for operation, shutdown, or start-up; or new computer control systems or programming. To ensure that changes do not result in inadvertent reactive chemicals events, all changes must be evaluated for the consequences.

Many companies, including Dow, have a formal “Management of Change” (MOC) policy. This is a structured work process to evaluate any change by knowledgeable experts for its consequences. Completion of the MOC process is required before any new chemistries, process changes, or procedures can be implemented. At the R&D scale, this MOC policy may sound burdensome, but the effort and review is scaled down to address the perceived risk associated with the reviewed activity and is appropriately and efficiently applied. This sometimes consists of simply requiring a conversation with at least one independent and knowledgeable colleague.

8. Conclusions: The Measure of a Good Reactive Chemicals and Process Safety Culture

The gauge of whether a Reactive Chemicals Program is successful or not can be based on some obvious parameters such as process safety performance, tracking unwanted events and near-misses. Clearly a successful program will show continuous improvement in performance over time. At another level, and perhaps harder to measure, is the degree of acceptance of the program by the employees. A truly successful program will be one in which employees not only accept the tenets of the program, but also thoroughly embrace the program for its value to the company in preventing reactive chemical events.

References

CCPS, 2008, The Public Version of Dow's Reactive Chemicals Program document was provided on CD to those purchasers of Guidelines for Hazard Evaluation Procedures, 3rd Edition**,** Center for Chemical Process Safety (CCPS), ISBN: 978-0-471-97815-2.

Frurip D.J., 2008, Selection of the Proper Calorimetric Test Strategy in Reactive Chemicals Hazard Evaluation, Organic Process Research & Development, 12(6), 1287-1292.

Frurip D.J., Elwell T., 2007, Effective Use of Differential Scanning Calorimetry in Reactive Chemicals Hazard Evaluation, Process Safety Progress, 26(1), 51-58.

Frurip D.J., Britton L., Fenlon W., Going J., Harrison B.K., Niemeier J., Ural E.A., 2004. The Role of ASTM E27 Methods in Hazard Assessment: Part I. Thermal Stability, Compatibility, and Energy Release Estimation Methods, Process Safety Progress, 23(4), 266-278.