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SAFETY ALERT

A Checklist for Inherently Safer Chemical Reaction Process Design and Operation

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The Center for Chemical Process Safety was established by the American Institute of Chemical Engineers in 1985 to focus on the engineering and management practices to prevent and mitigate major incidents involving the release of hazardous chemicals and hydrocarbons. CCPS is active worldwide through its comprehensive publishing program, annual technical conference, research, and instructional material for undergraduate engineering education. For more information about CCPS, please call 212-591-7319, e-mail ccps@aiche.org, or visit www.aiche.org/ccps

A Checklist for Inherently Safer Chemical Reaction Process Design and Operation

Introduction

Reactive chemistry incidents continue to occur in the chemical processing industry, and other industries which handle chemicals in their manufacturing processes. Some examples include:

- Lodi, New Jersey, 1995. An explosion during a blending operation resulted in five fatalities and destruction of much of the manufacturing facility[1].
- Columbus, Ohio, 1997. An uncontrolled reaction in a phenol-formaldehyde resin plant killed one worker, injured four others, and extensively damaged a plant[2].
- Paterson, New Jersey, 1998. A runaway reaction in a batch dye manufacturing process injured 9 people[3].
- Ringwood, Illinois, 2000. A decomposition reaction caused by water contamination and a failed pressure controller on steam tracing resulted in a pipe rupture. This relatively small incident resulted in no injuries or significant release of material, but did bring about an awareness of potential reactive chemistry hazards and plant modifications to prevent potentially more serious incidents in the future[4]. This incident also illustrates that many years of incident-free operation does not mean that there is no reactive chemistry hazard – this plant operated for over 40 years without incident until the wrong combination of events caused an unexpected chemical reaction which ruptured a pipe.

These and other incidents have resulted in increased attention to reactive chemistry issues by industry, government, and other stakeholders. The United States Chemical Safety and Hazard Investigation Board has completed a study of reactive chemistry accidents in the United States, and identified 167 serious incidents between January 1980 and June 2001[5].

Good process safety management systems, including consideration of reactive chemistry issues and the handling and storage of individual reactive chemicals, are important to operating a safe chemical process. This paper will focus on the technical aspects of safety in chemical reaction manufacturing processes, rather than management systems. In general, process safety management systems for reactive chemistry hazards are the same as for other chemical process hazards, and these are addressed in detail in many other publications of the Center for Chemical Process Safety. However, the implementation of process safety management systems for reactive chemistry hazards does require some specific tools and practices, some of which will be discussed in this paper. To help prevent future reactive chemistry incidents, we have summarized some basic engineering principles for safe operation of chemical reaction processes. Consideration of these principles will aid in the development of inherently safer chemical reaction processes.

Reactive chemistry hazards can result from any chemical reaction with the potential to release heat, pressure, or toxic reaction products in quantities too high to be absorbed or contained by the environment and equipment that holds the reacting mixture. It is important to distinguish between reactive chemicals and hazardous chemical reactions. The chemical substances in the process might not be considered to be reactive chemicals, but this does not mean that the process does not have reactivity hazards. Interactions of chemical substances may be more important for understanding process hazards than the reactivity of individual chemicals. Runaway reactions can occur from interactions among chemicals not considered particularly reactive by themselves.

The following checklist summarizes some important principles for design, scale up, and operation of chemical reaction processes. These principles are basic chemical engineering, but it is valuable to summarize them in one place so they will be easy to remember.

Chemical reaction hazard identification

1. **Know the heat of reaction for the intended and other potential chemical reactions.** There are a number of techniques for measuring or estimating heat of reaction, including various calorimeters, plant heat and energy balances for processes already in operation, analogy with similar chemistry (confirmed by a chemist who is familiar with the chemistry), literature resources, supplier contacts, and thermodynamic estimation techniques. You should identify all potential reactions that could occur in the reaction mixture and understand the heat of reaction of these reactions.

2. **Calculate the maximum adiabatic temperature for the reaction mixture**. Use the measured or estimated heat of reaction, assume no heat removal, and that 100% of the reactants actually react. Compare this temperature to the boiling point of the reaction mixture. If the maximum adiabatic reaction temperature exceeds the reaction mixture boiling point, the reaction is capable of generating pressure in a closed vessel and you will have to evaluate safeguards to prevent uncontrolled reaction and consider the need for emergency pressure relief systems.

3. **Determine the stability of all individual components of the reaction mixture at the maximum adiabatic reaction temperature.** This might be done through literature searching, supplier contacts, or experimentation. Note that this does not ensure the stability of the reaction mixture because it does not account for any reaction among components, or decomposition promoted by combinations of components. It will tell you if any of the individual components of the reaction mixture can decompose at temperatures which are theoretically attainable. If any components can decompose at the maximum adiabatic reaction temperature, you will have to understand the nature of this decomposition and evaluate the need for safeguards including emergency pressure relief systems.

4. **Understand the stability of the reaction mixture at the maximum adiabatic reaction temperature**. Are there any chemical reactions, other than the intended reaction, which

can occur at the maximum adiabatic reaction temperature? Consider possible decomposition reactions, particularly those which generate gaseous products. These are a particular concern because a small mass of reacting condensed liquid can generate a very large volume of gas from the reaction products, resulting in rapid pressure generation in a closed vessel. Again, if this is possible, you will have to understand how these reactions will impact the need for safeguards, including emergency pressure relief systems. Understanding the stability of a mixture of components may require laboratory testing.

5. **Determine the heat addition and heat removal capabilities of the pilot plant or production reactor.** Don't forget to consider the reactor agitator as a source of energy – about 2550 Btu/hour/horsepower. Understand the impact of variation in conditions on heat transfer capability. Consider factors such as reactor fill level, agitation, fouling of internal and external heat transfer surfaces, variation in the temperature of heating and cooling media, variation in flow rate of heating and cooling fluids.

6. **Identify potential reaction contaminants.** In particular, consider possible contaminants which are ubiquitous in a plant environment, such as air, water, rust, oil and grease. Think about possible catalytic effects of trace metal ions such as sodium, calcium, and others commonly present in process water. These may also be left behind from cleaning operations such as cleaning equipment with aqueous sodium hydroxide. Determine if these materials will catalyze any decomposition or other reactions, either at normal conditions or at the maximum adiabatic reaction temperature.

7. **Consider the impact of possible deviations from intended reactant charges and operating conditions.** For example, is a double charge of one of the reactants a possible deviation, and, if so, what is the impact? This kind of deviation might affect the chemistry which occurs in the reactor – for example, the excess material charged may react with the product of the intended reaction or with a reaction solvent. The resulting unanticipated chemical reactions could be energetic, generate gases, or produce unstable products. Consider the impact of loss of cooling, agitation, and temperature control, insufficient solvent or fluidizing media, and reverse flow into feed piping or storage tanks.

8. **Identify all heat sources connected to the reaction vessel and determine their maximum temperature.** Assume all control systems on the reactor heating systems fail to the maximum temperature. If this temperature is higher than the maximum adiabatic reaction temperature, review the stability and reactivity information with respect to the maximum temperature to which the reactor contents could be heated by the vessel heat sources.

9. **Determine the minimum temperature to which the reactor cooling sources could cool the reaction mixture.** Consider potential hazards resulting from too much cooling, such as freezing of reaction mixture components, fouling of heat transfer surfaces, increase in reaction mixture viscosity reducing mixing and heat transfer, precipitation of dissolved solids from the reaction mixture, and a reduced rate of reaction resulting in a hazardous accumulation of unreacted material.

10. **Consider the impact of higher temperature gradients in plant scale equipment compared to a laboratory or pilot plant reactor**. Agitation is almost certain to be less

effective in a plant reactor, and the temperature of the reaction mixture near heat transfer surfaces may be higher (for systems being heated) or lower (for systems being cooled) than the bulk mixture temperature. For exothermic reactions, the temperature may also be higher near the point of introduction of reactants because of poor mixing and localized reaction at the point of reactant contact. The location of the reactor temperature sensor relative to the agitator, and to heating and cooling surfaces may impact its ability to provide good information about the actual average reactor temperature. These problems will be more severe for very viscous systems, or if the reaction mixture includes solids which can foul temperature measurement devices or heat transfer surfaces. Either a local high temperature or a local low temperature could cause a problem. A high temperature, for example, near a heating surface, could result in a different chemical reaction or decomposition at the higher temperature. A low temperature near a cooling coil could result in slower reaction and a buildup of unreacted material, increasing the potential chemical energy of reaction available in the reactor. If this material is subsequently reacted because of an increase in temperature or other change in reactor conditions, there is a possibility of an uncontrolled reaction due to the unexpectedly high quantity of unreacted material available.

11. **Understand the rate of all chemical reactions.** It is not necessary to develop complete kinetic models with rate constants and other details, but you should understand how fast reactants are consumed and generally how the rate of reaction increases with temperature. Thermal hazard calorimetry testing can provide useful kinetic data.

12. **Consider possible vapor phase reactions.** These might include combustion reactions, other vapor phase reactions such as the reaction of organic vapors with a chlorine atmosphere, and vapor phase decomposition of materials such as ethylene oxide or organic peroxide.

13. **Understand the hazards of the products of both intended and unintended reactions.** For example, does the intended reaction, or a possible unintended reaction, form viscous materials, solids, gases, corrosive products, highly toxic products, or materials which will swell or degrade gaskets, pipe linings, or other polymer components of a system? If you find an unexpected material in reaction equipment, determine what it is and what impact it might have on system hazards. For example, in an oxidation reactor, solids were known to be present, but nobody knew what they were. It turned out that the solids were pyrophoric, and they caused a fire in the reactor.

14. **Consider doing a Chemical Interaction Matrix and/or a Chemistry Hazard Analysis**. These techniques can be applied at any stage in the process life cycle, from early research through an operating plant[6]. They are intended to provide a systematic method to identify chemical interaction hazards and hazards resulting from deviations from intended operating conditions.

Reaction process design considerations

1. **Rapid reactions are desirable.** In general, you want chemical reactions to occur immediately when the reactants come into contact. The reactants are immediately consumed and the reaction energy quickly released, allowing you to control the reaction by controlling the contact of the reactants. However, you must be certain that the reactor is capable of removing all of the heat and any gaseous products generated by the reaction.

2. **Avoid batch processes in which all of the potential chemical energy is present in the system at the start of the reaction step.** If you operate this type of process, know the heat of reaction and be confident that the maximum adiabatic temperature and pressure are within the design capabilities of the reactor.

3. **Use gradual addition or "semi-batch" processes for exothermic reactions.** The inherently safer way to operate exothermic reaction process is to determine a temperature at which the reaction occurs very rapidly. Operate the reaction at this temperature, and feed at least one of the reactants gradually to limit the potential energy contained in the reactor. This type of gradual addition process is often called "semi-batch." A physical limit to the possible rate of addition of the limiting reactant is desirable – a metering pump, flow limited by using a small feed line, or a restriction orifice, for example. Ideally, the limiting reactant should react immediately, or very quickly, when it is charged. The reactant feed can be stopped if necessary if there is any kind of a failure (for example, loss of cooling, power failure, loss of agitation) and the reactor will contain little or no potential chemical energy from unreacted material. Some way to confirm actual reaction of the limiting reagent is also desirable. A direct measurement is best, but indirect methods such as monitoring of the demand for cooling from an exothermic batch reactor can also be effective.

4. **Avoid using control of reaction mixture temperature as the only means for limiting the reaction rate.** If the reaction produces a large amount of heat, this control philosophy is unstable – an increase in temperature will result in faster reaction and even more heat being released, causing a further increase in temperature and more rapid heat release..... If there is a large amount of potential chemical energy from reactive materials, a runaway reaction results. This type of process is vulnerable to mechanical failure or operating error. A false indication of reactor temperature can lead to a higher than expected reaction temperature and possible runaway because all of the potential chemical energy of reaction is available in the reactor. Many other single failures could lead to a similar consequence – a leaking valve on the heating system, operator error in controlling reactor temperature, failure of software or hardware in a computer control system.

5. **Account for the impact of vessel size on heat generation and heat removal capabilities of a reactor.** Remember that the heat generated by a reactive system will increase more rapidly than the capability of the system to remove heat when the process is operated in a larger vessel. Heat generation increases with the volume of the system – by the cube of the linear dimension. Heat removal capability increases with the surface area of the system, because heat is generally only removed through an external surface of the reactor. Heat removal capability increases with the square of the linear dimension. A large

reactor is effectively adiabatic (zero heat removal) over the short time scale (a few minutes) in which a runaway reaction can occur. Heat removal in a small laboratory reactor is very efficient, even heat leakage to the surroundings can be significant. If the reaction temperature is easily controlled in the laboratory, this does not mean that the temperature can be controlled in a plant scale reactor. You need to obtain the heat of reaction data discussed previously to confirm that the plant reactor is capable of maintaining the desired temperature.

6. **Use multiple temperature sensors, in different locations in the reactor for rapid exothermic reactions**. This is particularly important if the reaction mixture contains solids, is very viscous, or if the reactor has coils or other internal elements which might inhibit good mixing.

7. **Avoid feeding a material to a reactor at a higher temperature than the boiling point of the reactor contents**. This can cause rapid boiling of the reactor contents and vapor generation.

Resources and Publications

There are many valuable books and other resources to help in understanding and managing reactive chemistry hazards. Some particularly useful resources include:

- American Institute of Chemical Engineers, Center for Chemical Process Safety, *Safety Alert: Reactive Material Hazards*, New York, 2001.
- *Bretherick's Handbook of Reactive Chemical Hazards*, Butterworth-Heineman, 1999.
- *Chemical Reactivity Worksheet*, U. S. National Oceanic and Atmospheric Administration, http://response.restoration.noaa.gov/chemaids/react.html
- American Institute of Chemical Engineers, Center for Chemical Process Safety, *Guidelines for Safe Storage and Handling of Reactive Materials*, 1995.
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Summary

We hope that the use of this checklist will help in developing, designing, scaling up, and operating inherently safer chemical reaction processes. This checklist includes many suggestions which have proven valuable in designing reactive chemistry processes over

the years. Like any checklist, it cannot cover all possible situations and circumstances, and it will be incomplete. We welcome suggestions to improve this checklist from readers based on their own background and experience. If you have suggestions for improvement, please e-mail them to ccps@aiche.org, and please let us know whether your suggestion may be included in future editions of this publication.

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5. *Improving Reactive Hazard Management*. Washington, D. C.: United States Chemical Safety and Hazard Investigation Board. October 2002 (Report No. 2001-01-H).

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