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Technique to Perform Petrochemical Complex-Wide Inadvertent Chemicals Mixing and Reactivity Study

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Abstract

Operating chemical plants require the delivery of chemicals from outside sources. According to the US National Association of Chemical Distributors, 40 million Tons of chemicals were delivered in 2016 to customers every 8.4 seconds. These chemicals may be in any phase or shape like solid, liquid or even gases. Chemicals transported into a petrochemical plant may be used as raw material, catalyst, water treatment or process treatment chemical etc. These chemicals may be hazardous by nature and may even be more hazardous upon unintentional mixing with each other or with process.

Among all the chemical transportation happening in a petrochemical plant, liquid chemicals for water or process treatment are of most interest due to the frequency of makeup, batch process, involvement of human action and hazardous nature of the chemical. Chemicals being transported via pipeline pose a lesser risk on inadvertent mixing and this is studied in detail in a normal HAZOP as misdirected flow etc. Solid chemicals pose a lesser risk due to less expected reactivity upon mixing and usually less frequent make up, loading and unloading.

In a typical Olefins complex, the count of chemicals with credibility of inadvertent mixing and hazardous reactivity may go as high as 30 chemicals. These chemicals include anti fouling chemicals, dispersants, acids, amines and proprietary chemicals. Credibility of inadvertent mixing of chemicals can help to shortlist the chemicals of greatest risk from inadvertent mixing.

Typically, the hazards of inadvertent mixing are studied within the boundaries of individual plants, while ignoring the credible scenarios of cross mixing from Plant A to Plant B within the same Petrochemical Complex.

This paper explains a proven technique to perform a complex-wide study of the chemicals mixing credibility and hazardous reactivity that reveals hidden risks, which may not otherwise be discovered through the typical process hazard analysis techniques like HAZOP of individual plants.

1 Introduction

There are typically many different operating units managed within a single petrochemical complex. Operating these units requires the delivery of chemicals from outside sources. According to the US National Association of Chemical Distributors over 400 billion tons of chemicals were delivered per day in 2016. These chemicals may be in any phase or shape like solid, liquid or even gases. Chemicals transported into a petrochemical plant may be used as raw material, catalyst, water treatment or process treatment chemical etc. These chemicals may be hazardous by nature and may even be more hazardous upon unintentional mixing with each other or with process. Among all the chemical transportation happening in a petrochemical plant, liquid chemicals for water or process treatment are of most interest due to the frequency of makeup, batch process, involvement of human action and hazardous nature of the chemical. Chemicals being transported via pipeline pose a lesser risk on inadvertent mixing and this is studied in detail in a normal HAZOP as misdirected flow etc. Solid chemicals pose a lesser risk due to less expected reactivity upon mixing and usually less frequent make up, loading and unloading. In a typical Olefins complex, the count of chemicals with credibility of inadvertent mixing and hazardous reactivity may go as high as 30 chemicals. These chemicals include anti fouling chemicals, dispersants, acids, amines, and proprietary chemicals. Credibility of inadvertent mixing of chemicals other than shortlisted chemicals may be ruled out based on the factors mentioned above.

Typically, the hazards of inadvertent mixing are studied within the boundaries of individual plants, while ignoring the credible scenarios of cross mixing from Plant A to Plant B within the same Petrochemical Complex.

2 Inadvertent Chemicals Mixing

Building an inadvertent chemical mixing credibility matrix is a good starting point for ensuring hazards are not missed during process hazard analyses (PHAs) and other risk assessments. Chemicals which are transported using entirely different transport mode may be excluded from credible mixing scenario. Likewise, chemicals, which have unloading connections very far away from each other, may be excluded as well. Hence, a shortlist of chemicals credible for mixing and hazardous reactivity may be made for detailed study. Focus should be on obvious **mixing and reactivity scenarios.**

2.1 Scope of Study

The scope of the following reactivity study includes chemicals present at the UNITED site as well as chemicals transported to/through the site to be unloaded. Lab chemicals and solids (pellets, powders, resins, etc.) are excluded from the reactivity study.

2.1.1 Types of Chemicals in a Petrochemical Complex

Different types of chemicals used in a petrochemical complex are given below.

Table 2.1. Chemical Categories and Criticality

Sr.#	Chemical Type	Transport Modes	Remarks
1	Water Treatment Additives	Mostly one way container such as 1 Ton-Eurotainer or iso tanker	Critical for inadvertent mixing
2	Process Additives-Liquid Catalyst	Mostly one way container such as 1 Ton- Eurotainer or iso tanker	Critical for inadvertent mixing
3	Raw Material, Product, Intermediate	Mostly piping	Not critical as mixing scenarios covered in conventional PHA
4	Lab Chemicals	Small Packing	Not Critical due to less quantity
5	Solid Chemicals, Catalyst, Desiccants, Filter Media,	Drums or bags	Not critical for inadvertent mixing
6	Utilities	Mostly piping	Not critical as mixing scenarios covered in conventional PHA

2.2 Chemicals Mixing and Reactivity Matrices - Data Collection

The complete list of chemicals, locations, normal drainage points and flows, overflow or uncommon points and flows, known and measured compositions and reactivities, and associated documents (matrices, SDS, incident reports, field measurements, detector data, etc.).

For proprietary chemicals, chemical supplier input is required to understand the true nature of the chemical and its reactivity. In standard safety chemical datasheets (SDSs), Section 10: Stability and Reactivity gives useful information about each chemical reactivity, stability, possibility of hazardous reaction, incompatible materials, and hazardous reaction products. See Figures 2.2.1 and 2.2.2 for examples for chemical compatibility matrices.

Figure 2.2.1 – Credibility of mixing chart

Inadvertent Chemicals Mixing Credibility Chart																							
Sr. #	**Plant**	**Chemical Name**																					
1	Unit-1	Chemical-A1	1																	✓	Credible		
2		Chemical-A2	✓	2																x	Not Credible		
3		Chemical-A3	x	x	3																		
4		Chemical-A4	x	x	✓	4																	
5		Chemical-A5	x	x	✓	✓	5																
6		Chemical-A6	x	x	x	x	x	6															
7	Unit-2	Chemical-B1	x	x	x	x	x	x	7														
8		Chemical-B2	✓	✓	x	x	x	x	✓	8													
9		Chemical-B3	x	x	x	x	x	x	✓	✓	9												
10		Chemical-B4	x	x	x	x	x	x	✓	✓	✓	10											
11		Chemical-B5	x	x	x	x	x	x	✓	✓	✓	✓	11										
12		Chemical-B6	x	x	x	x	x	x	✓	✓	✓	✓	✓	12									
13		Chemical-B7	x	x	x	x	x	x	✓	✓	✓	✓	✓	✓	13								
14		Chemical-B8	x	x	x	x	x	x	✓	✓	✓	✓	✓	✓	✓	14							
15		Chemical-B9	x	x	x	x	x	x	✓	✓	✓	✓	✓	✓	✓	✓	15						
16		Chemical-B10	x	x	x	x	x	x	✓	✓	✓	✓	✓	✓	✓	✓	✓	16					
17		Chemical-B11	x	x	✓	✓	x	x	x	x	x	x	x	x	x	x	x	x	17				
18		Chemical-B12	x	x	✓	✓	x	x	x	x	x	x	x	x	x	x	x	x	✓	18			
19		Chemical-C1	x	x	✓	✓	x	x	x	x	x	x	x	x	x	x	x	x	✓	✓	19		
20	Unit-3	Chemical-C2	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	20	
21		Chemical-C3	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	✓	2
22		Chemical-D1	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	✓	✓

Figure 2.2.2 – Reactivity Matrix

Inadvertent Chemicals Mixing Consequence Chart (Generic)

Sr. #	Plant	Chemical Name																					
1	Unit-1	Chemical-A1	1																				
2		Chemical-A2	PU	2																			
3		Chemical-A3	x	x	3																		
4		Chemical-A4	x	x	U	4																	
5		Chemical-A5	x	x	PU	PU	5																
6		Chemical-A6	x	x	U	U	U	6															
7	Unit-2	Chemical-B1	x	x	x	x	x	x	7														
8		Chemical-B2	U	H	x	x	x	x	H	8													
9		Chemical-B3	x	x	x	x	x	x	H GT	U	9												
10		Chemical-B4	x	x	x	x	x	x	H	U	U	10											
11		Chemical-B5	x	x	x	x	x	x	H GT	PU	U	PU	11										
12		Chemical-B6	x	x	x	x	x	x	H GT	PU	U	PU	PU	12									
13		Chemical-B7	x	x	x	x	x	x	U	U	U	U	U	U	13								
14		Chemical-B8	x	x	x	x	x	x	H GT	U	U	C	U	U	U	14							
15		Chemical-B9	x	x	x	x	x	x	U	U	U	U	U	U	U	H E	15						
16		Chemical-B10	x	x	E F	E F	x	x	x	x	x	x	x	x	x	x	x	16					
17		Chemical-B11	x	x	GT	H GT	x	x	x	x	x	x	x	x	x	x	x	H GT	17				
18		Chemical-B12	x	x	x	x	x	x	H	x	x	x	x	x	x	x	x		H	18			
19	Unit-3	Chemical-C1	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		19		
20		Chemical-C2	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		U	20	
21		Chemical-C3	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		GF H	U	21

Consequence
C= Cancer Causing
E= Explosion
H= Heat Generation
F= Fire
U= Unknow but Hazardous
GT= Toxic Gas Formtion
GF= Flammable Gas Formation
PU= Process Upset

2.3 Brain-storming Part of Inadvertent Mixing Study

The Chemical Mixing and Reactivity Study Technique is good for data collection and for some of the brainstorming, in What-If/Checklist fashion. But it is good to supplement this with freer brainstorming method such as 'What if'. Risk ranking of the top credible inadvertent mixing and hazardous reactivity scenarios is advised for a focused and cost-effective risk mitigation. Risk ranking basis include likelihood/frequency of the chemicals interacting, specific composition and quantity of the chemical storages, severity of the mixing consequences etc. A multi-discipline team, including process engineer (chemical engineer), operation specialist, process safety engineer/EHSS representative, local facility or corporate chemical reactivity SME, and where applicable a chemical supplier representative should all be included in the analysis process; with operators, process engineers being key roles for the allowable minimum team members required determine the risk involved in each (credible) mixing scenario. The team composition will likely change if multiple units are involved, having the appropriate operators and process engineers for each mixing scenario. When a risk score for each scenario is established, available safeguards should be evaluated to determine the residual risk of mixing. If there is unacceptable residual risk after considering the available safeguards, new recommendations should be generated and implemented for each mixing scenario for final mitigation of the risk. Typical available safeguards include written SOPs, chemical labelling, operators experience, etc. More effective recommendations to bring the mixing hazard risk to acceptable level include adding safeguards such as: providing dissimilar unloading connections, providing proper spacing between unloading connections, adding clear labeling and avoid congested unloading points, installing captive key arrangements for top credible mixing chemical locations/scenarios, etc. See Figure 2.3.1 for an example of a What-If analysis worksheet for inadvertent mixing.

Figure 2.3.1 – Example of risk analysis results (worksheet)

Sr #	Mixing Chemicals	Location	Credibility	Frequency of Make up	Mixing Causes	Mixing Consequences	Consequence Score	Mixing Probability	Risk Level	Exising Safeguards	Recommendations
1	Chemical A1 + Chemical C2	Unit 3	Credible due to similar Mode of transport within same plant and similar transport container (iso tank)	Weekly	Escort mistakenly leads truck to wrong location and connected to the tank	Hazardous reaction that may generate heat, splattering or boiling and toxic vapors	Moderate	Likely	High	SOPs, Operational practices and experience, labeling, different nozzle types (confirm)	Improving labeling at both locations. Re-confirm different design of nozzles. Consider adding lock and key arrangement for HCl unloading point.

Human factors are of utmost importance in the chemical unloading operations in a chemical plant. If the design and layout of procedures do not clearly indicate what should be done, the resulting confusion can increase the potential for error. Accordingly, the inclusion of job aides, such as checklists, into procedures can help ensure critical steps are adhered to. The extent to which facility operators train their personnel on procedures, and verify knowledge and skills, can also affect the potential for error.

Because systems and procedures do not always work as intended, it is critical for companies to examine them regularly and effectively through active monitoring. With meaningful employee participation, procedures can be written or updated to align with actual operator performance, where appropriate. When actual practice is found to deviate from procedures in an unsafe way, such as having truck drivers perform hose line hook-ups without operator verification, then supervisory instruction, training, and verification to adhere to the procedures is needed.

In most cases, as at MGPI Processing[2], relying on administrative controls to prevent inadvertent mixing is not enough. The site should evaluate and provide any necessary independent protection layers (IPLs), since human error probability cannot be less than 1/100 per task. These can include some of the safeguards listed in Table 2.3.1 below.

Table 2.3.1 Example from one Company of Different Types of Additional Protection Layers (APLs) (beyond administrative controls); some are Independent Protection Layers (IPLs)

Type	Specifics	Risk Reduction Factor	For …*	Cost, $K
Bar Code /Scanner	Bar Code – w/o procedure imbedded; combined with interlocks	3-10	OE/MD	0.1 per
Bar Code /Scanner	Bar Code – with procedure imbedded; combined with interlocks	3-10	All	0.3 per
Proof Switches	RFID (radio frequency identification; the reader is hardwired)	100	OE/MD	5 per
Proof Switches	Proximity Limit Switches (both ends are hardwired)	10-100	OE/MD	0.5 per
Hardware	Stand-alone valve (spring loaded dead-man valves; for quick draining/venting)	10-100	OE	0.2 to 1 per
Hardware	Dry disconnects (auto-closing valve on hose end designed to have no leaks on disconnection)	10-100	OE	TBD
Hardware	Automated/interlocked valve (typically to eliminate hose)	100	OE/MD	1 to 10 per valve
Hardware	Captive Key	100	OE/MD	0.5 to 1 per

* OE = Open Ended; MD = Misdirected

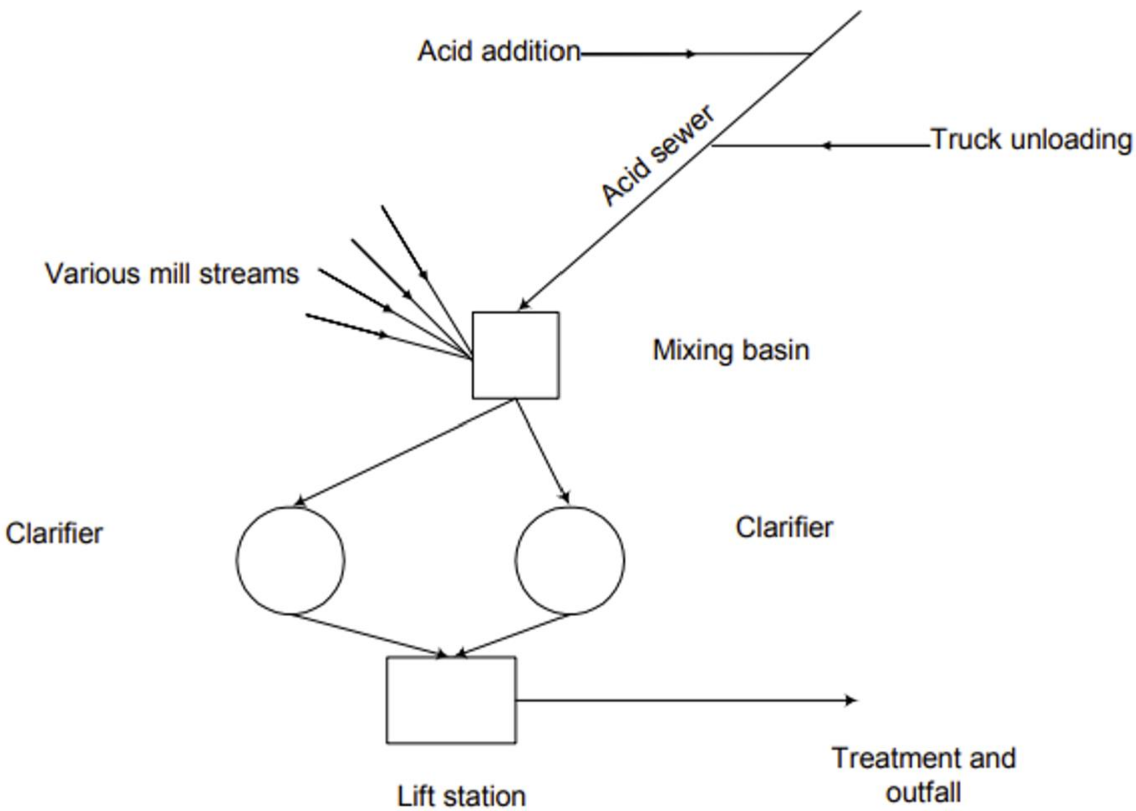
2.4 Sewer & Drainage Pit Studies

Sewer related chemical reactivity incidents have historically occurred across many industries. Therefor facilities which manage reactive chemicals, especially those which can combine and liberate toxic or explosive gases from spills or due to draining vessels into sewers or pits should preform an additional or separate analysis of the sewer system itself. For example, in plants in which organics and acids could mix in open sewers and generate deadly hydrogen sulfide gas[6] this hazard may require additional safeguards, given this is a credible scenario. With proper data gathering and field work it is possible to produce a thorough facility sewer reactivity study, using documented chemical locations, their drainage destinations or sewer systems to generate potential credible scenarios. This process involves cares consideration of sewer and open pit/open sewer headers. A typical approach for conducting systematic and through analysis is listed in the US EPA reference document: *Guidance to Protect POTW Workers from Toxic and Reactive Gases and Vapors*[7].

> <u>EXAMPLE of Application of EPA Guidance:</u> Figure, 2.4.1, below, shows a basic diagram of the sewer system for a paper mill in Florida, US, where a release of H2S from process sewers resulted in the deaths of 2 contractors and injured eight others (CSB report, 2002 [6]). This details flaws in the sewer system, including

later connections made to the sewer system which were not properly evaluated as part of the Management of Change (MOC) process, as well as several many other design, management and process Safety Management (PSM) gaps. Such diagrams and sewer maps should be proactively considered with regards to chemical reactions (weighed against credibility matrices, etc.), especially if scenario of inadvertent mixing could be catastrophic.

Figure 2.4.1 CSB illustration of 2002 Neheola H2S release incident – sewer/wasterwater diagram (Fig 1, pg 21 [6])



3. *Conclusion*

- Combined safety study of chemicals unloading operation within industrial facilities may reveal hidden risks, which may remain undiscovered if we only rely on the prevalent process hazard analysis techniques like HAZOP of individual plants. Scope of such studies should be the overall complex, not the individual plants. The scope such analysis should include proper PSI and related tools needed in generating as many scenarios as possible; this is to include sewer reactivity and other drainage design studies.

- Building strong Workforce Competency on PSM, including topics such a Reactive Chemicals Management is of paramount importance to today industrial facilities. This proper execution of such programs relies heavily on knowledge of other elements, such as MOC and Human Factors (HF). Generally, the importance of training personnel in HF awareness and consideration in evaluating of risk can't be overstated. Chemical unloading operations rely entirely on humans to be performed. All the engineering safeguards and best available hierarchy of control should be made available to minimize the risk, understanding that humans are in these cases not IPLs.
- Continuous improvement in training and SOPs is required all the time to avoid chemical unloading incidents. Learning from incidents is very crucial in avoiding similar mistakes. Adequacy study of chemical unloading equipment should be done to highlight any deficiency in the available equipment and configuration.
- Emergency response plan and equipment should be reconsidered based on the chemical mixing and reactivity study to include any deficient emergency response equipment or gap in the design or emergency plan.
- 100 % compliance to the written SOPs all the time every time. But also provide engineering safeguards against the human errors that will inevitably occur.
- Perform PHA of procedures for loading and unloading to find the scenarios that are unique to these batch operations and to ensure there are IPLs for the human errors that can (and will) occur.
- Always adhere to the required PPEs while handling any chemicals, while also ensuring there are sufficient engineering safeguards to prevent releases and mixing.
- Outside drivers should not be allowed to do unloading connections, as they may not be fully aware of the nature of inadvertent mixing and hazardous reactivity. Access to the chemical unloading location should be restricted to fully trained personnel only. In addition to the EHSS consequences, inadvertent chemical mixing may also involve production losses and sustainability losses. For example, a wrong chemical unloaded into a closed cooling water system may result in loss of huge quantity of treated water and plant shutdown for several days.
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