FILES

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RE: LAD CMP Reactive Chemical Module

Louisiana CMP, as a result of the 1995 consolidated audit process, decided to develop a reactive chemical IPT module for the plant. Attached is a hard copy of the module, as well as a disk containing the file, for your information.

Hopefully this module is in a format, or contains information, that will be applicable to you. We consider this to be a "live" document, and will handle revisions internally. Gary Rizzo, CMP's Training coordinator, is the owner of the document and is responsible for ensuring it stays updated. Vic McMurray is the CMP Reactive Chemical Contact.

Sincerely,

Kevin J. Kelley
CMP Production Engineer

CONFIDENTIAL

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CMP RESOURCE
REACTIVE CHEMICAL PROGRAM INFORMATION
RESOURCE

PURPOSE	To provide information to the individual on the Dow Reactive Chemicals Program, Special Concerns for the Methanes Plant, past reactive chemicals incidents applicable to CMP, special hazards associated with each plant area, and lines of defense protecting against an incident.
SCOPE	This document will explain the purpose of the Reactive Chemicals Program and specific reactive hazards of materials used at CMP.
RELATED EQUIPMENT	Entire Chlorinated Methanes Plant Facility
DEFINITIONS	Defined within module
CONCERNS	The Reactive Chemicals Program is one of Dow's primary Loss Prevention Tools. The program is designed to increase awareness and always question the potential hazards associated with materials and processes that become commonplace in day to day operations. The reactive chemicals review process is a continuing review that addresses safety, health, and environmental issues.

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To access a particular section of this document, double click on the specified box.

MODULE SECTION SELECTION MENU

Reactive Chemicals Program Overview

Methyl Chloride Unit Concerns

Methylene Chloride/Chloroform Unit Concerns

CMP Reactive Chemical Special Concerns

Past Reactive Chemicals Incidents

REACTIVE CHEMICAL RESOURCE MODULE

About this Module:

This module was developed as a follow up item to the 1995 Consolidated Audit. In an effort to heighten reactive chemical knowledge, and to focus the collective knowledge of the Chlorinated Methanes Plant, this module was developed. It should be kept up to date as more reactive chemical knowledge is acquired.

The method of presentation throughout this module will be the following:

Event:	Description of reactive chemical event that occurs
Operating deviation:	Action or situation that occurs that causes the reactive chemical event.
Consequences:	The result of the deviation. Describes possible effects on personnel, equipment, etc.
Lines of Defense:	Description of systems that are in place to prevent reactive chemical event and protect in case it does.

It is important to understand all of the situations known as a **CONSEQUENCE OF DEVIATION** from normal operation. Understanding the lines of defense that are in place is the key to preventing reactive chemical events.

K.J. Kelley
Author, 10/95

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THE REACTIVE CHEMICALS PROGRAM

The Reactive Chemicals Program is a review process designed to prevent unwanted chemical reactions from taking place. This is done by TRAINING, REVIEWING, and TESTING. The program is designed to ensure all plant personnel are aware of the reactive chemical hazards of the area in which he or she works. The Reactive Chemical Review Program is a critical part of a PROCESS HAZARD ANALYSIS (PHA). PHA's are completed for existing processes, changes in a processes (MOC process), and in new processes.

Each plant has a designated REACTIVE CHEMICAL CONTACT. The contact is responsible for ensuring training takes place, incidents are communicated, and reactive chemical potential is reviewed for changes in processes.

DESIGNATED REACTIVE CHEMICAL CONTACT: **Vic McMurray (as of 10/95)**

Most of the Reactive Chemical incidents which occur in Dow facilities are repeats of those which have occurred in the past. Incidents are well documented in the REACHEM reactive chemicals data base program. For more information on access, contact the plant reactive chemical contact. Nearly all Dow reactive chemical incidents involve chemistry that is very well known. In most cases, procedures are available when dealing with reactive chemicals or materials, but good judgment must be used. Always contact supervision immediately if you suspect an unwanted chemical reaction may be underway. In many cases, quick action will avert a very serious incident.

The basic components of a good reactive chemical review include the following:

1. Review of credible scenarios for plant areas-

CREDIBLE SCENARIOS (Realistic events that could take place) are considered for each area of the plant. Examples of credible scenarios include tube leaks, control valve failures, flow swings, instrument failures, etc. The LINE OF DEFENSE (how we are protected from the event) for each scenario is discussed to ensure protections systems and procedures address the situation. An example of a line of defense is shutting down the Thermalchlorination Reactor, R-1300, if the differential pressure between the chlorine and the organic sides gets too low. This prevents organics from backing into the chlorine header, causing an explosion (see M2/M3 Unit Concerns for more info). The alarms warning low differential prior to shutdown are also considered lines of defense.

2. Review past reactive chemical events-

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A list of past reactive chemical events for materials and processes common to the CMP process should be researched. CMP has a reactive chemical file and a reactive chemical binder in which results of past reviews and past incidents are kept. Events and test results should always be shared with Operations, Staff, and the Tech Center when possible. Past events should be analyzed to see if a credible scenario at CMP exists which could produce a repeat of the event.

3. Review Chemical and Material Specific Reaction Hazards-

The specific hazards of each chemical or specialty material used at (or potentially entering) the block must be reviewed. For example, the potential reaction between Aluminum and chlorinated organics is very well known. However, numerous incidents have occurred due to M1 compressor parts constructed of aluminum.

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REACTIVE CHEMICALS IPT MODULE
M1 PRODUCTION UNIT CONCERNS

PURPOSE: To familiarize you with the specific reactive chemical hazards of the M1 Production Unit. This includes HCl Purification, Methanol storage, Hot Oil area, R-250's, quench, drying, condensing, finishing, and storage of methyl chloride.

HCl Purification Area:

Event:	**Reaction between hydrocarbon oils and HCl in K-55**
Operating deviation:	D-60 refilled with hydrocarbon based oil instead of CP-1000.
Consequences:	HCl and hydrocarbon oils will react creating carbons and evolving heat. This can cause damage to K-55 due to solids. Also, solids in the system may cause a K-55 seal failure and an HCl spill. Early warning may come from strange peaks on C-70 O/H analysis.
Lines of Defense:	1. "Oil" program on PDP-11 specifies CP-1000 synthetic oil. 2. Periodic oil samples taken.

Event:	**Extensive corrosion due to water in system**
Operating deviation:	Vessel put in service without checking dewpoint. Wet oil added to K-55 system.
Consequences:	Water entering the system will cause severe corrosion and damage equipment. Spills are possible, and damage to the entire division HCl system (Solvents, CMP, Vinyl II) is possible.
Lines of Defense:	1. HCl system piping and valves always dried (purging or baking). 2. Oil sampled in compressor system to monitor for impurities.

R-250 Reaction Area

Event:	**Bis-chloromethylether formation in R-1300**
Operating deviation:	C-202 overhead temperature becomes greater than 40 C. C-202 looses circulation, allowing DME (dimethyl ether) to pass overhead.
Consequences:	When C-202 recirculation is lost, make up acid flow is too low, or C-210 malfunctions allowing a high C-202 overhead temperature DME carryover can occur. This will cause high levels of DME in the crude M1 that is used in R-1300. When DME passes through the thermal chlorinator, it reacts to form

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	Bis-chloromethyl ether (also known as Bis). Bis is a highly toxic material that distills with M2. Since some emissive uses for M2 exist, people could possible be exposed.
Lines of Defense:	1. CMP runs 20% excess HCl in the hydrochlorination reactors. This maximizes reaction selectivity to M1, thus forming less DME. 2. An on stream analysis is run for DME with alarms set to notify operator if levels are high (> 5 PPM). 3. C-210, the cooling column, greatly unloads C-202. Gas is cooled from 40 to 25 C in C-210. Heat generated in C-202 during the absorption of water is less likely to cause a high overhead temperature on C-202 due to the cooler starting temperature. 4. Alarms are used to warn operations: C-202 midsection temperature > 35 C High temperature on packed sections Low density alarm on C-202 bottoms acid Sulfuric make up and recirculation low flow alarms

Event:	**Insulation Fire on R-250's**
Operating deviation:	Oil leaks into insulation surrounding the R-250's.
Consequences:	The autoignition temperature of Shell Thermia C hot oil is normally 340 C. If an oil leak develops in the R-250 hot oil system, the oil can saturate insulation. When this occurs, the surface area the oil encompasses greatly increases compared to the same amount of oil in a pool. This reduces the autoignition temperature. If conditions are correct, the oil saturated insulation may catch on fire and cause major damage to the area.
Lines of Defense :	1. Operations rounds in R-250 area to look for leaks each shift. 2. Training on the hazards of autoignition depression. 3. TDC alarms for hi/lo flow and D-470 drum level (major leak) 4. Foam fire protection system in place in the event a fire takes place.

Event:	**Alumina catalyst reaction with air during recharge**
Operating deviation:	Catalyst is dumped without being properly wet down during removal.
Consequences:	Alumina dumped from the hydro reactors will absorb great amounts of water from the air. During absorption, heat will

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	be generated. This will increase the temperature of catalyst to the point at which traces of hydrocarbons left on the catalyst can begin to burn. The decomposition can cause a fire in waste containers and give off HCl, possibly exposing personnel.
Lines of Defense:	1. Reactor recharge procedures utilized to ensure reaction potential is minimized. 2. Catalyst is water soaked during the disposal procedure. 3. Wastes are properly labeled and disposed.

Event:	**Lack of quench water causes corrosion and Hydrogen evolution**
Operating deviation:	R-250 reactors started up without proper quench flows R-250 reactors started up with C-202 running
Consequences:	Starting up without quench water will cause a large water load on C-202. This will overload the column causing heat generation (from absorption of acid) and will cause very low acid concentrations in the top part of C-202 which is carbon steel. 60-70 % H_2SO_4 is extremely corrosive and will attack the carbon steel, and release hydrogen. This hydrogen will end up in vent recovery and the dry vent header. Hydrogen in this header could cause a major explosion at the THROX if large amounts are present.
Lines of Defense :	1. Start up procedures require good quench flow. 2. Alarms in place: * Low recirculation flow * High temperature on quench columns * Low H_2SO_4 density

Event:	**Loss of hot oil in hydrochlorination reactors leads to run away reaction or severe corrosion**
Operating deviation:	Hot oil flow to R-250 reactors is greatly reduced due to loss of one or more P-470.
Consequences:	Hot oil provides 2 things to the R-250 system (1) The heat of reaction is removed from the reactors. If the hot oil flow is reduced, the temperature of the isothermal section of the R-250's will begin to increase. The temperature of the adiabatic section will also increase. As reactor temperatures increase, so will the rate coke formation on the catalyst. As temperatures climb, the catalyst can become coked over and deactivate. It is possible that at very high localized temperatures, high rates of corrosion can cause pitting of reactor tubes and other damage to the vessel

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(2) The feed materials are superheated by the hot oil flow. If this flow is reduced or eliminated, temperatures downstream of the superheater could drop below 185 C. If the heat tracing doesn't keep pipe wall temperatures hot, there will be severe corrosion to the inlet piping downstream of the static mixers.

Lines of Defense :

1. Spare off line pump is available if an on-line one malfunctions.
2. Reactor Trips- If the adiabatic section temperatures exceed 350C, the reactor will automatically trip. The reactor will be swept with Nitrogen to stop further coke formation.
3. Alarms in place:
   * Low Hot oil flow
   * High reactor outlet temperature
   * Low inlet reactor temperatures.

M1 Finishing and Storage Area:

Event: **Eruption of Methyl Chloride Caustic Filter**
***** Note: This incident occurred at CMP, May 1992 *****

Operating deviation: Water is left in a filter after the filter is washed instead of totally draining out the vessel.

Consequences: Flake caustic is sometimes used to remove trace HCl from finished methyl chloride. These filters have to periodically be recharged with fresh caustic. If the filter is not free of water before new caustic is added, this event occurs. The heat of absorption as the water absorbs the caustic will cause a great amount of localized heat. If the flake caustic traps the water beneath, the water can quickly become steam. This steam expands quickly and blows a slurry of flake caustic and caustic solution out of the vessel. Extreme damage to eyes and skin is possible. The force of the eruption can also hurt someone if they (or a piece of equipment) is in the way when it occurs.

Lines of Defense :

1. Detailed recharging procedures have been developed for M1 filters.
2. New M1 condensing and finishing column system prevents the need for the caustic filters. Any residual HCl is removed by distillation now.

Event: **Methyl Chloride reaction with Aluminum**
***** Note: An incident occurred in 1994 when an aluminum baffled tank truck was loaded at CMP.**

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(See past events section for more information)

Operating deviation: Process equipment, piping, or valving made from aluminum comes in contact with Methyl Chloride.

Consequences: Methyl chloride (as well as any other chlorinated solvent) reacts with aluminum at a very high rate. The methyl chloride reaction creates a "pyrophoric" material (spontaneously combusts when exposed to oxygen). If the material is exposed to oxygen, is will begin to heat up and will catch on fire. Methyl chloride is a very flammable gas. The results of a methyl chloride/aluminum reaction is usually total destruction of a piece of equipment. This incident has occurred hundreds of times in aluminum containing methyl chloride offload compressors.

Even if M1 and aluminum have reacted in a vessel, a fire may be prevented by protecting the system from oxygen exposure. Very detailed disposal procedures have been used in the past when this occurs.

Lines of Defense :

1. Training - Contractor, operations, and engineers are taught the hazards of aluminum and methyl chloride.
2. Design specifications - Piping specifications and equipment specifications are noted about the hazard of a using aluminum.

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REACTIVE CHEMICALS IPT MODULE
M2/M3 PRODUCTION UNIT CONCERNS

PURPOSE: To familiarize you with the specific reactive chemical hazards of the M2/M3 Production Unit. This includes Thermalchlorination, condensing, refrigeration, distillation and storage in the M2/M3 area .

Thermalchlorination Area:

Event:	**Liquid Chlorine carry over causes explosion in R-1300**
Operating deviation:	Liquid chlorine enters R-1300 feed system due to entrainment of droplets from high level in S-1301.
Consequences:	R-1300 reaction is controlled by adjusting the chlorine content in the feed. The reactor normally runs 22-23 mole % chlorine in the feed. Operation above about 30 mole % causes the reactor to enter the "flammability range" a range at which M1 and M2 react in an explosive manner with Chlorine. This can cause a detonation in the reactor or, more likely, in the mixing nozzle, N-1300. When liquid droplets carry into the mixing nozzle, the localized mole % of chlorine enters the flammable range, causing the exothermic reaction. The reactor control system should trip (see below) the reactor, but if it doesn't the potential for detonation in the mixing nozzle N-1300 is high.
Lines of Defense:	1. Self limiting electric heat tracing on reactor feed lines and vessel. Maintains header temperature above dewpoint (not designed to vaporize incoming liquids) 2. Mod 5 alarms/trips: * High level alarms/trips on S-1301 * Mixing nozzle temperature (trip reactor if > 120 C) * High reactor outlet temperature trips

Event:	**High Chlorine mole % causes operation within flammable range.**
Operating deviation:	Feed streams varied to R-1300 such that chlorine mole % of feed streams cause the mixture to become explosive. This can occur when 2 phase feeds feed the reactor, or if the control system enters a swing.
Consequences:	R-1300 has an on-line flammability calculation that uses the temperature, pressure and feed concentrations of streams to R-1300. The flammability is a correlation of how close the

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	mixture feeding the reactor is to its explosive point. The typical range is 70-80% with 100% meaning concentrations have entered the explosive range. If the reactor enters this region, the reaction could "run away" and cause detonation, possible equipment damage, and a spill.
Lines of Defense:	1. On line flammability calculation, utilizing redundant flow meters 2. Mod5 Code to adjust feed composition and eventually trip as % of Flammability increases.

Event:	**R-1300 Inlet line exotherm**
Operating deviation:	Conditions exist that are conducive to an exotherm during start up or running conditions. An improper M1 sweep during start ups or chlorine on the organic side of the mixing nozzle are examples of deviations from normal operations.
Consequences:	1. Improper M1 sweep: During a reactor start up, M1 is swept through the mixing nozzle for 2 reasons. (1)To cool the nozzle in order to prevent extremely quick reactions in the nozzle and (2) Remove ferric chloride which acts as a catalyst that quickens the reaction rate of M1 and Chlorine. If the M1 isn't swept long enough, these conditions can cause an inlet line exotherm. 2. Chlorine on organic side of mixing nozzle: During start up, a good differential pressure (> 50 psig in normal) is necessary to ensure proper chlorine distribution into the mixing nozzle. Condensing train pressure should run low to maximize the DP. This prevents locally high chlorine/organic ratios (which cause exotherms). Just prior to the introduction of chlorine, the chlorine side of the nozzle is swept with HCl to ensure there are no organics on the chlorine side of the nozzle.
Lines of Defense:	1. Mod5 automated start up. 2. Purges are part of start up code 3. DP alarms (<10 psi) and reactor trips (5 psi) to prevent backing up organics into chlorine header. 4. Mixing nozzle temperature trips to detect nozzle exotherms.

Event:	**Fire in R-1300 during maintenance work**
Operating deviation:	R-1300 is opened and exposed to oxygen instead of maintaining an inert purge on it during work.
Consequences:	When R-1300 is shutdown and opened up for maintenance, the carbon bricks will remain hot for several hours, possibly days. The carbon, if exposed to oxygen at high temperatures,

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will burn. This could lead to destruction of all of the R-1300 internals (bricks, rectifier elements, thermocouples) and would be an extremely hazardous situation for a person to be near.

Lines of Defense:
1. An inert purge if R-1300 is worked on without cooling to ambient temperatures.
2. Training on the scenario.

Chlorine Header System:

Event: **Improper materials of construction used with Chlorine system causing equipment damage or spill.**

Operating deviation: Improper materials of construction during maintenance or modifications to the chlorine header.

Consequences: Using the wrong materials of construction in Chlorine service almost always leads to a reactive chemical event. Titanium and Chlorine react very violently. Graphoil gaskets eventually decompose and create a major spill hazard. Valves must be properly prepared for Chlorine service (all traces of oil from manufacturing removed). Usually, equipment in chlorine service with improper materials of construction is severely damaged and a spill occurs. Potential exposure to Chlorine is a serious health hazard.

Lines of Defense:
1. Titanium not used in block piping or vessels.
   * Only exception is distributor in C-751, chlorine scrubber on THROX).
   * Maintenance personnel trained on hazards and a statement about the hazards of titanium is in block indoctrination.
   * Titanium parts are normally painted purple for hazard identification in material management group.
2. Fluorolube is used in pressure transmitter diaphragms
3. Pipe specs are strictly adhered to for piping systems. (MOC policies identify deviations and modifications, ensure properly prepared valves are utilized.)
4. Chlorine iron fire protected against by self limiting electrical heat tracing.
5. Gylon gaskets used on chlorine system flanges.
6. PTFE tape or Loc-tite PTFE sealant used on piping (no "Never-seize" used in Chlorine system.
7. Only tested and approved leak sealants used.

Event: **Ammonia flash fire during Chlorine piping leak tests**

Operating deviation: Improper ammonia solution utilized for leak checking chlorine

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	system.
Consequences:	Using solutions of ammonia in water greater than 6% ammonia can cause a flash fire. When the system is leak checked and chlorine is present, the ammonia and chlorine react and give off a very visible "smoke" cloud. However, if the ammonia concentration is too high, the water present isn't enough to prevent a small fire from taking place. The HCl given off also can irritate the person performing the tests.
Lines of Defense:	1. Only a stock solution, supplied by Langley, is utilized at CMP. It is a 6% solution. 2. Operations trained to utilize only this stock solution for leak detection.

Distillation Area:

Event:	**Chlorine/methylene chloride reaction is D-1525 ("Soak Tank")**
Operating deviation:	Due to an upset in distillation, a high concentration of methylene chloride in the soak tank.
Consequences:	If M2 concentrations are > 0.5%, there is a risk of the initiation of the thermalchlorination reaction to M3. If chlorine concentrations are high enough, the reaction could go out of control and overpressure D-1525, causing the safety valves to relieve.
Lines of Defense:	1. D-1525 Chlorine concentration is analyzed 1/shift to ensure concentrations are < 1000 ppm. 2. D-1525 and C-1520 bottoms are GC sampled, including analysis for M2 (maintain < 100 ppm). 3. Chlorine control valve utilizes small Cv to minimize chance of incident.

Event:	**V-1515 Molecular Sieve exotherm**
Operating deviation:	V-1515 is put on line or recharged improperly. (1) The bed is lined up very quickly, instead of slowly as it should be. (2) When the mole sieve is dumped from the bed, it is improperly handled.
Consequences:	(1) When a fresh molecular sieve bed is put on line for the first time, it should be done slowly. If it isn't, the heat of absorption of chemicals into the mole sieve could cause a rise in pressure and possible release. If a slow, but constant flow is maintained, the heat generated is dissipated and this isn't a problem.

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	(2) Molecular sieve beds are dumped after regeneration isn't working anymore. If molecular sieve is dumped without properly wetting down the sieve, there will be heat produced from the absorption of water from the air. As this occurs, carbon deposits and trace trapped chemicals on molesieve can begin to smolder and catch on fire if not identified.
Lines of Defense:	(1a.) Procedures detail the need to slowly put V-1515 on line. (1b.) Bed temperatures monitored and alarmed on Mod5. (2a). Recharge procedures highlight reactive chemical potential.

Product Finishing:

Event:	**Chloroform and caustic react and overpressure filter vessel**
Operating deviation:	HCl removed from Chloroform by using a caustic filter.
Consequences:	Caustic and chloroform are one of the worst possible combinations found at CMP. The reaction is extremely exothermic and can easily cause a vessel to overpressure (and overheat metal). Caustic filters are not used in M2 service due to the small concentration of M3 in M2.
Lines of Defense:	1. Caustic filter not used at CMP for methylene chloride lights removal. C-1530 is used for M2 stripping. 2. Training on hazard of reaction.

Storage Area

Event:	**Fire in PSA (Pressure Swing Absorption) unit filter beds**
Operating deviation:	A PSA bed is suddenly fed a high concentration of organics or oxygen enters the PSA bed.
Consequences:	As organics are absorbed, they evolve heat. Due to the expanded surface area of the carbon used for organic absorption, the temperatures needed to begin burning organics can be depressed to around 150 C. If oxygen is present due to leaks in the vacuum system or improper vacuum breaking with air, a PSA carbon bed can quickly catch fire.
Lines of Defense:	1. Bed temperatures are used to monitor, alarm, and shutdown PSA units (Mod5 controlled). Bed temperatures are on the critical instruments system. 2. Vacuum breaking is done with nitrogen to ensure that oxygen levels in the system stay low. 3. Oxygen analyzer on PSA-1770 (methanol tanks) to identify and alarm high O_2 levels in the beds and prevent an exotherm.

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Event:	**Fire during recharge of PSA Carbon beds.**
Operating deviation:	A PSA unit bed is recharged without properly grounding handling equipment or is dumped without adequate soaking of spent carbon.
Consequences:	When a PSA bed is dumped, the dust particles can create a large static charge. If the static isn't handled via grounding, a spark could ignite the carbon when in the presence of air. Trace flammables in the carbon could cause a fire. As the beds are dumped, the carbon will begin to absorb water from the air. As this happens, heat is given off. This heat, coupled with the expanded surface area of the carbon used for organic absorption can result in the carbon catching on fire.
Lines of Defense:	1. Recharging procedures detail need to properly ground equipment. 2. Recharging procedures detail the hazard of absorption during a recharge of the carbon beds. Carbon is water soaked as it is slowly dumped from the beds.

REACTIVE CHEMICAL RESOURCE MODULE

SPECIAL CONCERNS FOR THE METHANES PLANT

Purpose: To discuss specific special reactive chemical concerns for the Chlorinated Methanes Plant. This includes waste handling (>50% of all reactive chemicals incidents), Loading hazards, leak repair, and raw material identification methods.

Waste Handling

Event:	**Unwanted/unknown reaction in waste collection containers.** ***** Note: CMP had a reactive chemical event handling waste, January 1992 *****
Operating deviation:	Possible deviations to normal procedures are Waste not solidified, Mixed with other waste, or Solidified with wrong material.
Consequences:	Over half of all reactive chemical events occur due to improper waste handling. It is always important to (1) identify the waste, (2) understand its chemical potential, and (3) dispose of according to strict procedures. If waste streams are mixed or solidified with the wrong materials, usually heat and a gas are given off. If the materials are in a sealed container, the container may overpressure, rupture and could spill its contents in an undesirable place. Sometimes, extremely explosive materials can be made in incorrectly handled waste containers.
Lines of Defense:	1. CMP training on waste disposal. 2. CMP utilizes only *Oil Sorb* brand absorption material for solidifying CMP waste streams. It has been tested with CMP chemicals and waste streams and has shown no reaction.

Loading Area Hazards:

Event:	**Unknown or unwanted reaction in a railcar or barge due to reaction of product load with heel.**
Operating deviation:	Tank car, tank truck, or barge loaded without a heel sample taken.
Consequences:	Many customers utilize process vent streams to create pressure and off-load tank cars. This is not recommended, but it still happens. When this is done, the remaining liquid or vapor (the "heel") will contain some compounds that are not normal to our plant. This may also happen when a car, truck,

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	or barge is used in multiple services. If a material, such as caustic were left over, and chloroform as loaded on top of it, the results could be a major reactive chemical event.
Lines of Defense:	1. All tank cars and barge heels are sampled (even if there is just vapor heel on a car. All questionable chemicals identified are checked for compatibility. 2. Detailed checksheets and procedures are utilized by loading personnel to ensure checks such as these are made.

THROX Area Hazards

Event:	**Improper chemicals in THROX vent header causes major corrosion or explosion**
Operating deviation:	Below is a list of materials vented to an incorrect THROX header: (1) Oxygen is in the dry vent header (2) Chlorine in the dry vent or wet vent header (3) Methanol is in the dry vent header
Consequences:	(1) Oxygen in the dry vent header can cause formation of a flammable/explosive mixture in the header. This could react very violently in the header, or at the THROX. More than likely, water will be produced. This will lead to major corrosion damage to the header piping. (2) Chlorine in the dry or wet vent can react with organics and reach explosive reaction rates. A Thermalchlorination reaction (-25 kj/mol) is possible. (3) Methanol in the dry vent header will react with HCl and form water and methyl chloride. The water produced can lead to major corrosion damage of the piping system and D-751.
Lines of Defense:	1. Procedures and signs at THROX drops detail the hazard of venting an improper material to an improper drop. 2. The methanol loops from the R-250 start up bleeds are hard piped to the wet vent header. 3. Chlorine is vented through a separate header to the THROX, or is scrubbed at the tail scrubber. The chlorine header is hard piped to the burner.

Event:	**Propylene Oxide polymerizes in dry vent drum D-751**
Operating deviation:	Cellulose waste from T-39, containing propylene oxide, is accidentally routed to D-751 through the liquid feed manifold.
Consequences:	If improper valving allows T-39 waste to enter D-751, propylene oxide in the waste can begin to polymerize in the presence of HCl. This could cause a pressure excursion in the dry and would likely create a need to replace exposed

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	equipment.
Lines of Defense:	1. Double block and bleed in place for liquid from Cellulose. 2. Only one liquid is burned at a time in R-750. This prevents possible combination of liquid streams. 3. Training of operations on hazards of P.O. in D-751.

Raw Material Identification:

Event:	**Improper raw material is used causing product contamination or an unwanted reaction.**
Operating deviation:	Incoming raw material not properly identified. Paperwork absent or incorrect on raw materials.
Consequences:	If unknown chemicals are utilized in the process, the results will be exactly that... unknown. Problems could range from minor product contamination to a major exothermic reaction, causing equipment damage.
Lines of Defense:	Raw materials entering CMP are positively identified. Consult lab sample procedures for the most correct identification methods.

Leak Sealant:

Event:	**Improper leak repair chemical is used causing product contamination, an unwanted reaction, or a large spill.**
Operating deviation:	Using a leak repair sealant or material of construction that has not been tested and accepted within the company as acceptable.
Consequences:	If unapproved leak sealants are utilized in the process, there is a very high risk that much larger spill could occur.
Lines of Defense:	Leak repair sealants are tested and approved by the LAD reactive chemicals department. CMP leak clamps use sealants that are listed on the division's approved list. This list is posted and maintained on the VAX Cluster and is owned by R&D.

REACTIVE CHEMICAL RESOURCE MODULE

REACTIVE CHEMICALS IPT MODULE
PAST INCIDENTS COMMON TO THE METHANES PLANT

Purpose: To highlight reactive chemicals events from the past that could potentially, or did, occur at the Louisiana Division Methanes Plant. (Note: a current incident list can be obtained from the REACHEM data base. Contact reactive chemical contact for more information).

January 1992: Reaction between H_2SO_4 waste stream and fly ash. - CMP incident
* Fly ash was used to neutralize and solidify a waste stream from D-750. The mixed materials reacted, overheated, bubbled and caused the drum to overflow materials onto the ground.

May 1992: During a caustic filter recharge, caustic erupts from vessel, exposing CMP operator. - CMP incident
* During the recharge of the M1 filters, flake caustic was dumped from a hopper into a filter. The filter contained residual water from the washing process. The heat of absorption caused vaporization of some of the water. A 60' jet of caustic shot from the filter, spraying the operator. Luckily his head was turned away as he dumped the filter, avoiding major exposure to his face and avoiding the hopper that was blown out of the way by the plume.

February 1991: Incident 91-0010 Inspection prevents untagged air hose from being used for drying Chlorine system. (non-CMP incident)
* During a concrete rehab program, a procedure was put in service so that hoses used on pneumatic hammers were tagged red. During an inspection it was found out the contractor used an untagged hose. The hose contained oil. If it would have been used to dry equipment in chlorine service, a major reaction would have taken place between the oil and the chlorine.

July 1980: Incident 80-0043 Activated alumina bed fire - non CMP incident
* An activated alumina bed at the Vinyl II plant had been out of service for three months. The vessel was opened for recharge. Ten hours later, a fire occurred in the activated alumina bed. The exothermic absorption of moist air on alumina ignited organics in the bed.

February 1982: Incident 82-0009 Exotherm during cooldown of methanol hydrochlorination reactor

REACTIVE CHEMICAL RESOURCE MODULE

* An exotherm occurred during the cool down of a methanol hydrochlorination reactor at the Chlorinated Methanes Plant. The adiabatic section temperature rose from 250 to 438 C. Methyl chloride was being used to cool the reactor when the excursion occurred. It is suspected that localized clumping of catalyst in the bottom of the reactor allowed the reaction to "run away" in one area due to poor heat dispersion and flow paths.

January 1990: Incident 90-0002
Chlorinated Methanes Explosion (Freeport plant)
* The Chlorinated Methanes plant experienced a reactive chemical loss when the "run" chlorine transmitter read full scale flow even though the line was manually blocked in. This "apparent flow" caused an automatic shutdown. The chlorine EBV's closed. One minute after shutdown, an explosion occurred in the chlorine line between the reactor and EBV's. Cause of the explosion was backmixing of methyl chloride into the blocked chlorine line.

June 1994:
* Aluminum Baffled tank truck loaded with methyl chloride - CMP incident
A new tank truck supplier was used for the transportation of methyl chloride. The supplier, unknowingly supplied CMP a truck with aluminum baffles. Poor knowledge of his own equipment was the root cause. The methyl chloride formed a pyrophoric aluminum alkyl within the truck. Through very detailed procedures, the explosive mixture was safely handled and disposed of without further incident.