CAUSTIC 1 / CHLOR-ALKALI 2

1997

REACTIVE CHEMICALS REVIEW

QUESTIONNAIRES

1997 REACTIVE CHEMICALS REVIEW (CAUSTIC AND CAII)

REVIEW OF REACTIVE CHEMICALS CONCERNS

This section provides a detailed format within which to conduct a self-audit of the process(es) under review. There are 23 sections that cover various aspects of plant operations that have Reactive Chemicals concerns and/or issues. With each section there are one or more places for you to add notes that are pertinent to your process. Previous Reactive Chemicals incidents have been included for most of the 23 sections.

A. EVALUATION OF REACTIVE CHEMICALS DATA
The objective of these questions is to determine if the appropriate test data have been obtained and appropriate safeguards provided. Refer to the Process Flow Sheet and Test Summary Data.

a. Have Reactive Chemicals test data been gathered and evaluated for the following:

Yes	No	
[X]	[ ]	Process materials and mixtures that are normal to the operation;
[X]	[ ]	Mixtures that may result from abnormal conditions;
[X]	[ ]	Materials of construction throughout the process;
[ ]	[X]N/A	Potential sources of flammable dusts tested/explosive range known; rate of pressure rise data;
[X]	[ ]	Accelerating Rate Calorimetry (ARC) test on reactive mixtures and formulations that are handled in drums or larger volumes;
[X]	[*]	Auxiliary materials, e.g., cooling tower chemicals that are normal to the operation;
		Are changes in the following entities tested:
[X]	[*]	Chemical components
[X]	[*]	Significant changes in concentrations, in formulations
[X]	[ ]	Materials of construction?
[X]	[ ]	Vent Sizing Package (VSP) run on reactors/tanks containing reactive materials.

Additional Comments: [*] N/A for Caustic

b. Do all individuals involved with reactive chemicals evaluation understand the information on the data sheets and know the limitations for extrapolating operating parameters from the data? What kind of training have they had?

Response(s): Individuals involved with interpretation of reactive chemicals data are either knowledgeable from past experience or trained on understanding the data by the individuals in the division who provide the data and/or reactive chemical experts in the division. All members of the department have been trained on the Vital Reactive Chemicals Issues for the Chlor-alkali Technology. They have participated in scenario training to insure the application of the knowledge. In addition, they have been trained on Chempat-compatibility charts, incident

reviews, reactive chemicals audit results, and reactive chemical matrices associated with chemical compatibility as well as chemical/material of construction compatibility.

c. Have existing reactive chemicals data been reviewed to ensure that they are still appropriate to the process under consideration. In particular, consider the following:

Response(s): Reactive chemical data has been reviewed. This was recently performed during the generation of the chemical and material of construction compatibility matrices for the technology.

Does it thoroughly define hazardous bounds? Yes, see Vital Process Safety Considerations especially as related to Reactive Chemical concern.
Has the process been checked out with a material balance flow diagram? A material flow diagram does exist for the plants. Although they have not recently been reviewed (last review in prior to June 1995 installation of new fin-fan intercoolers for the CAII Chlorine Plant), there have been no significant modifications to the technology which would indicate a need for a thorough review especially as concerns Reactive Chemicals.
Do data include total potential energy available in case a runaway reaction occurs? Yes.
Have test data been reviewed with Reactive Chemicals Testing and updated? All Reactive Chemicals test data is generated in the Louisiana Division or through the LAD Reactive Chemicals group. It is assumed that all data generated is added to the Reactive Chemicals Testing database.
When? As data is generated Who? By data generator and plant engineer
Does your system have the capability to adequately remove heat in a worst case situation?

Response(s): Caustic Production: If a situation were to occur, all heat (steam) would be cut and available chilling/cooling would be utilized. Chlorine Production: If a situation were to occur, the chemical and heat source would be eliminated as practical, with external water applied as the situation allows to mitigate the heat generated by the incident. Mod 5 will automatically quench the taffy pot contents with liquid Cl_2 if an exotherm is detected.

B. CONFIRMING ANALYSIS OF RAW MATERIALS

a. Is there a program in place for chemically confirming all raw materials; are you comfortable with a Certificate of Analysis being required and received for those raw materials difficult to test? Do your suppliers manufacture look-alike chemicals that are different and could possibly be put in a mislabeled container by mistake?

Response(s): (1) Most raw materials are supplied via Dow partners. The partners are responsible for positive ID of the materials (Raw Brine [Analyzed weekly for nitrogen-bearing compounds], Treated Brine, Sulfuric Acid [Checked for color and specific gravity at Division Chlorine before the incoming tank cars are off-loaded to storage.], Hydrochloric Acid and Carbon Tetrachloride [checked by Solvents and communicated to CAII Room]. Vendor supplied materials such as solvents, oils, lab chemicals, boiler treatment chemicals, etc., are accepted with Certificates of Analysis. This is deemed adequate because there are no significant reactive chemical concerns associated with the process and these vendor supplied chemicals. Procedure followed for positively identifying Sodium Thiosulfate and Sodium Bisulfite. (2) Yes, but stringent labeling requirements as well as knowledgeable operations personnel have been sufficient to manage this situation.

b. Are inhibitor levels tested on in-coming raw materials that require an inhibitor? Have you worked with your suppliers of raw materials on specifications and potential contaminants?

Response(s): (1) N/A Inhibitors are not used on incoming raw materials. (2) Due to GMP, this has been done with respect to the Chlorine Plant and Power & Utilities.

c. What level of training do analysts receive; are the analytical data for raw materials unambiguous; are there materials that could give similar analytical data?

Response(s): Most raw materials are received via dedicated pipelines and, as stated above, no identification testing is done. Analysts in the department receive the training described in A.b. Data that is received/generated is unambiguous in nature. Operators are trained to I.D. Sodium Thiosulfate and Sodium Bisulfite using off loading procedure.

C. MATERIALS OF CONSTRUCTION

a. Has the process been reviewed for appropriate materials of construction with respect to operating conditions? Does the Tech Center provide information and/or recommendations for materials of construction? Is information sought from suppliers of raw materials?

Response(s): (1,2,3) Yes, this has been recently reviewed during the generation of the reactive chemicals compatibility chart relative to materials of construction. This is also achieved via equipment and piping specifications. The Tech Center reviewed the compatibility chart and reviews all pipe specs for the technology. Plant changes which are outside of the equipment and pipe specifications are addressed via MOC and involve Engineering and Tech Center review prior to implementation. Raw material suppliers are utilized as needed for information of this nature as well.

b. Is testing required just prior to installing parts to assure the correct material of construction? Are materials used such as lubricants, thread compound, instrument filling fluids, etc., compatible with the process?

Response(s): (1) Inventory Management and the Maintenance Department have been given access to the Reactive Chemical concerns associated with the Chlor-Alkali process. They perform training for workers and insure that only proper materials are used via this training as well as policies and procedures. Specialty parts, such as titanium, are segregated and clearly identified. (The procedure requires positive ID [via Texas Nuclear] of titanium.). Access to the parts is limited. Very little actual testing is performed though specifications clearly dictate appropriate materials. (2) Materials which have been found to be compatible with the process are utilized. Training includes data on these issues.

c. Are undesirable materials of construction identified, controlled (by whom? Yes, by Inventory Management and CA&D Maintenance), and communicated (to whom? Personnel utilizing the material as well as pipe and material specifications and procedures)?

d. Are materials monitored for corrosion in the process? Are conditions that can cause corrosion in the system well known?

Response(s): (1) Yes, via the Pressure Vessel Program and associated visual and thickness checks as well as the PSM Piping Integrity inspections. (2) Yes, via technical knowledge as well as pipe specifications and caustic soda service graphs.

D. SIDE REACTIONS

Have side reactions in your process been adequately researched and identified? Have conditions for unwanted reactions been identified such as pH, water, contaminants, H2 evolution, unusually lengthy temperature excursions? Is any part of your process or storage subject to peroxide, acetylide or azide formation? If so, are the sources known and a program in place to keep this under control?

Response(s): (1, 2, 3) N/A for caustic. (1, 2) All addressed for CAII and engineering controls and system process monitoring are in place to provide early warning of potential unwanted reactions. (3) No peroxides, acetylides or azides exist as part of the process.

E. SCRUBBERS [X] NA (for Caustic Production)

a. Is backflow of the scrubber into the process possible? Is it possible to create an unwanted vacuum on the process from the operation of the scrubber? Are two or more process vessels relieved to a common scrubber?

Response(s): (1) No. (2) No, a seal pot is in place. (3) Yes, with respect to the chlorine high pressure scrubber.

b. Can flammable or reactive materials accumulate in the scrubber medium or vapor space? Can the vent stream overcome the scrubber on very high flow?

Response(s): (1) Vacuum relief devices prevent hydrogen inclusion into the chlorine. (2) No.

c. How is the scrubber medium monitored to assure its effectiveness?

Response(s): pH control determines if we are adding enough caustic to scrub chlorine (and keep some excess alkalinity in the effluent) and not form chlorates which has a higher heat of reaction.

F. CATALYSTS [X] NA Except as noted below.

a. Where does the catalyst in the process end up? Can it become a hazard? Is it in the Material Balance? Can catalytic activity be lost, poisoned or inhibited such that reactants could be charged without reacting. Are all potential reactions known for improper flows or conditions across the catalyst bed?

Response(s):_____

_____

b. Is the catalyst checked before loading a new batch? Does a new or fresh catalyst bed require a special procedure?

Response(s):_____

_____

c. What are the procedures for starting up a catalyst bed or molecular sieve bed? Do they prevent a plug-flow type temperature front?

Response(s):_____

_____

d. Can the material of construction cause a catalytic effect with the product? Are there any components in the product that can react with the material of construction and cause catalytic problems? Can iron enter the process causing a hazardous catalytic effect or stop the reaction; can FeCl3 be made by an acid condition? Can rust from carbon steel vessels become a potential source of unwanted catalyst?

Response(s): Yes, at CAII, moisture excursions can cause FeCl3 formation thus acting as a catalyst for unwanted reactions on non-fully chlorinated components such as CHCl3. This issue is understood and moisture monitoring and alarming is in place to prevent/warn of such occurrences.

G. INHIBITORS [X] NA

a. Are inhibitor levels monitored? How are they monitored? Is the inhibitor affected by materials of construction or vice versa?

Response(s):_____

_____

b. Is inhibitor effectiveness temperature dependent or can cold temperatures cause separation of the inhibitor from the product? Does the inhibitor require a small amount of oxygen to be effective? If so, is it monitored so as to avoid being eliminated by nitrogen padding?

Response(s):_____

_____

H. ENVIRONMENTAL CONTROLS

a. How are the mixing of waste streams monitored for unwanted reactivity?

Response(s): pH control systems exist on outfalls and ditches. Excess hypochlorite/sulfite levels are also monitored and controlled.

b. How are carbon adsorption beds, pressure swing absorption units (PSA's), etc. monitored for correct operation?

Response(s): N/A

I. LAB CHEMICAL STORAGE

a. Is there a policy governing ownership responsibility, and date of receipt, for chemicals being stored; is a log or chemical inventory kept; is disposal or transfer of ownership of chemicals and samples required when the current owner is transferred?

Response(s): Procedures are in place to define ownership, receipt of materials requirements, etc. Chemical inventory is controlled by the Analytical Leader on MSMS and managed by the Consolidated Lab personnel. Transfer of ownership is not documented.

b. Are unstable chemicals given special storage provisions; is moisture a problem with some chemicals you store? Are your chemicals stored by compatibility or alphabetically?

Response(s): There are not unstable chemicals. All chemicals are stored by compatibility utilizing good laboratory practices.

J. HAZARDOUS MATERIAL HANDLING - POTENTIAL CONSEQUENCES (This section is N/A to Caustic Production)

a. Is the material you handle subject to heat of compression hazard? If so, what procedures are in place to prevent explosions when opening valves/starting pipeline flows?

Response(s): No.

b. Can material be concentrated or built up in a recycle stream to the point of instability? Can polymer or other materials in the process build up and become pyrophoric when exposed to air; is oxygen monitored in process systems where a component can be easily oxidized; are any peroxide-forming materials and conditions present in your process? If so, how is this controlled?

Response(s): (1) Yes. Nitrogen trichloride produced in the system is diluted using carbon tet and purged regularly to the Solvents plant for destruction. (2) No pyrophoric potential exists. (3) Oxygen levels in the hydrogen system are monitored. (3) No peroxide-forming conditions exist.

c. Can any of the materials, when contacted with a high surface area substrate, result in a lowering of the auto ignition temperature to a hazardous range?

Response(s): Hot oil leaking onto porous insulation is an issue in the exhaust tunnel of the gas turbine where the main turbine oil pump is located. The area is insulated with "Kao-wool" material, which is one of the few materials adequate for this service conditions. Oil leakage here is sure to ignite in a short period of time with metal temperatures in a range of 700 - 900 degrees F. Temperature monitoring and alarming systems exist in the exhaust tunnel of the turbines as well as steam injection which can be activated when high temperature conditions exist. In addition, the turbine will runback on high disc cavity temperature. There is also an issue associated with the bone char in T-603. The concern is associated with exposing the bone char to air during disposal. Although there are no plans to dispose of the char, if disposal is ever planned, a procedure will be developed to address avoiding spontaneous ignition problems.

d. Can prolonged storage of any material lead to a hazardous situation?

Response(s): No.

K. WASTE HANDLING

a. Are the absorbents used in your area selected on the basis of test data? Are procedures in place to prevent spontaneous ignition with absorbents and filters? Any prohibited absorbents? Has everyone been trained on this?

Response(s): Test data does exist and is used when making choices of absorbents or changes to absorbents currently used. There are no issues with spontaneous ignition other than those discussed in J.c. There are no prohibited absorbents and personnel are aware of the absorbents to be used. Procedure exists in Procedure library.

b. Are different waste chemicals collected in a common container? If so, what are the controls over what is put into the container? Does control of waste include materials of construction; time limit of storage; written procedure for disposal.

Response(s): Waste handling procedures are in place and annual training occurs. Waste characterizations define container requirements including mixing of containers (such as in the lab). Procedures define storage time when this is an issue.
Describe your procedures: Wastes are packaged as required by RCRA regulations and waste characterization instructions.

L. HEELS IN TANK CARS, TRAILERS, LINES, VESSELS, AND BARGES
Are heels, resulting from cleaning, a hazard with your products? Are procedures in place to analytically test all heels before making transfers? Are vapors in pressurized vessels/trailers analyzed if no liquid sample can be obtained? Are dedicated transport vessels used without confirming heel identity? If so, how do customer and vessel handling procedures ensure the contents of the returned vessel?

Response(s): (1)Yes: With respect to caustic tank cars and trucks, preloading checklists insure that heels are identified prior to loading. With respect to the cleaning of chlorine lines/vessels/equipment, systems are dried after cleaning. (2) No. (3, 4) There are dedicated vessels for transporting caustic. This equipment must have paperwork communicating last-contained material. Procedures are in place to allow early detection of heel problems.

M. EXCHANGERS [] NA

	Yes	No	
a.	[X]	[ ]	Does the failure of any heat transfer system result in an uncontrollable condition? Have you evaluated the effects of recirculation or cooling failure?

Response: N/A for Caustic. For CAII, a chlorine/iron fire can result from loss of heat transfer associated with the chlorine compressor fin fans. This system is monitored for this issue.

b. Is the exchanger medium compatible with the process material? Will cross-contamination with the process be hazardous; is monitoring provided to detect a leak?

Response(s): Caustic Production: (1) Yes (2) No (3) Yes - Testing is performed daily per routine sampling and testing schedules. Chlorine Production: Exchangers exist with chlorine and freon/ chlorine and water. While chlorine and freon are not incompatible, cross contamination is not desirable and is analyzed. Cross exchange of chlorine and water is in a process area where the water pressure exceeds the chlorine pressure (and Cl2 is already wet), minimizing the impact of a leak (E-201/202).

c. Is temperature monitoring provided around the exchanger? Has the reboiler's maximum temperature been evaluated with respect to time/temperature exposure to the material being vaporized?

Response(s): Caustic Production: (1) Yes, (2) No, this is not a reactive chemicals concern in caustic production; Chlorine Production: (1, 2) Yes.

N. AGITATORS [X] NA

a. Has agitator failure (power failure) been evaluated during the step with the most available energy to determine if a runaway can occur? Is monitoring provided to detect agitator failure? Are reactive feed flows interlocked to stop on agitator failure?

0. STATIC MIXERS [X] NA

Can overheating occur within the static mixer if flow of reactants is suddenly stopped without purge-out? Are temperatures before and after the mixer monitored?

P. PUMPS

a. How are all pumps protected from deadheading? Does the monitoring scheme assure detection and alarm/SD on pump cavitation? If not, how is this detected and controlled? Are feed pumps interlocked with shutdown trips?

Response(s): Caustic Production: (1) Operating discipline (2) No. (3) Operator rounds and Flow data available to the control room operator. (4) Some such as cooling booster pumps.

Chlorine Production: (1) Operating discipline (2, 3, 4) P-510 chlorine pumps have elaborate monitoring on MOD 5 with alarms to help prevent overheating and a chlorine/iron fire. Pumps must be manually tripped from the field switch or the breaker. EBV's on the suction and discharge of the liquid chlorine pumps also serve as a line of defense for minimizing chlorine losses if a pump ruptures.

b. Have recycle streams been evaluated for loss of recycle? Can extended time agitation lead to an unacceptable temperature rise? Is a reaction controlled by pumping through a heat exchanger?

Response(s): (1) Yes (2) No (at CAII, P-510 chlorine pumps can be manually shutdown upon alarm indication of a problem. (3) No.

c. Are pump seals monitored for flow of seal fluid and seal loss; would a seal fluid leak into the process be a reactive chemicals hazard?

Response(s): (1) Yes, by operator rounds, (2) No.

d. Are there installations in the process where pumps are used for mixing? If so, has there been an evaluation of the effectiveness of mixing? Can unreacted materials be forwarded to undesirable places due to poor mixing?

Response(s): (1) No, (2) N/A, (3) No

Q. BACKFLOW
Have potential backflow scenarios been evaluated; has process backflow been effectively prevented in feed lines, nitrogen connections, condensate, gas cylinders? Is redundancy of protection provided?

Response(s): Caustic Production: (1) Yes, backflow scenarios have been evaluated. There are adequate safeguards in place at the caustic user plants to prevent organics from backing into the caustic header. Since there are no crossties in caustic manufacturing, there are no issues associated with gas cylinders and/or nitrogen connections. Condensate quality is monitored. (2) Since there is no issue in caustic production, there is no need for redundancy protection and it therefore does not exist. Chlorine Production: (1) Yes, primary concern in the cell area; Hydrogen in chlorine; chlorine in hydrogen, air in hydrogen. (2) The concern and potential of these situations is well understood and training on these issues occurs regularly. Redundancy protection is provided.

Describe your backflow protection: In general, use of check valves, double block and bleeds and intermediate tanks with level monitoring. In the chlorine cell area; gas composition monitoring, cell header vacuum relief device and cell head operating discipline and monitoring and well as hydrogen header EBV's.

R. FLOW RATE, DISTILLATION

a. Have low and high flow rates been evaluated for their effects on reaction stability and heat removal? If the control valve is fully open will this flow rate result in a hazardous situation?

Response(s): (1) Yes, these conditions have been evaluated and are defined per Consequences of deviation from normal operating conditions. Warning of the conditions are per control system alarms. (2) No reactive chemical concerns.

b. Has total reflux of your distillation columns or reactor systems been evaluated for loss of overheads through leaking overhead valves? Concentration of unstable components in certain trays?

Response(s): No reactive chemical concerns.

S. RELIEF DEVICES AND VENT SYSTEMS

Have relief devices been calculated for worst case reactive chemicals runaway; two-phase flow? Are relief device vent systems common to more than one system? If so, has the system been sized for back pressure when one or more than one reactor overpressures?

Response(s): (1) Relief devices have been calculated for worst case and two-phase flow considerations. (2) For Caustic Production, there are no common vent systems; but these do exist in Chlorine Production. (3) Process engineering evaluations have been completed concerning pressure drop and no reactive chemical concerns exist.

T. COMPATIBILITY CHART

Has a current cross-compatibility chart been developed for chemicals used in the block that may be mixed unintentionally; are self-reactive materials and materials of construction, included in the data? Is the compatibility chart posted where all block employees can use it? Are employees trained in its use? Is there a policy for keeping the cross-compatibility chart up to date?

Response(s): (1, 2, 3, 4) Yes to all of the above questions. During 1996, chemical compatibility matrices were generated for the process. A matrix was developed for each of the following: process chemicals, lab chemicals, cell crew lab chemicals and materials of construction. The chemical compatibility workbook resides on the Procedure library network where it can be accessed by all employees. It is defined as a critical document such that a hard copy is also available to employees.

U. REACTIVE CHEMICALS TRAINING AND SCENARIOS

a. Is a training module developed for Reactive Chemicals in the department? Is reactive chemicals training conducted/tested/documented? Is attendance checked for those needing training?

Response(s): (1, 2, 3) Yes to all above. Operator plant area IPT modules include some reactive chemical training as well as in the IPT module for new/transferring employees. All members of the department have been trained on the Vital Reactive Chemicals Issues for the Chlor-alkali Technology. They have participated in scenario training to insure the application of the knowledge. In addition, they have been trained on Chempat-compatibility charts, incident reviews, reactive chemicals audit results, and reactive chemical matrices associated with chemical compatibility as well as chemical/material of construction compatibility.

Describe your training program and provide the most recent documentation: Training is required to be performed annually (per the C-9 checklist; assigned to the Production Leader). During 1996 training was performed in July. In addition, mini-training opportunities are taken during the year as Global Reactive Chemicals communications issue which pertain to our plants.

b. Does reactive chemicals training include materials specific to the block; have hazard envelopes of chemical mixtures that are reactive/flammable/explosive been developed and included in the training program; are case histories of past incidents in your unit, the Dow

world, and the chemical industry, related to your process, included in the training program; have potentially wrong mixtures or procedures been emphasized.

Response(s): Yes to all above.

c. Are important parameters, such as pH, water, contaminants, similar analyzer peaks, assurance of exotherm onset, side reactions, etc. included in periodic training; are employees trained on the ways instruments and control devices are prone to fail?

Response(s): Yes to all above. Fail safe considerations are reviewed. Periodic scenario training addresses these issues.

d. Are employees drilled on scenarios covering reactive chemicals concerns with written corrective procedures and/or responses for process upsets? If so, how often and which shifts?

Response(s): Quarterly drills are held for each shift. In the past, reactive chemical considerations have been included in drill scenario's. During 1996, two of the drill scenarios included reactive chemical considerations.

V. CUSTOMER INFORMATION/PRODUCT STEWARDSHIP

a. Are customers informed of potential reactive chemicals hazards of products/formulations? Is the customer information current; are changes in formulations or concentrations communicated to the customers?

Response(s): Yes to all above. MSDS sheets as well as the Caustic Handbook covers these issues well. Any changes in formulations or concentrations beyond stated specifications are communicate to the customers.

b. Is assistance offered to the customer to pursue reactive chemicals concerns; do you assure yourself that the customers understand the data provided; are materials of construction concerns communicated to the customer?

Response(s): Yes to all above. The plants do assist with the communication of this information to the customer though the primary ownership for these areas lies with TS&D, Marketing and Logistics.

W. REACTIVE CHEMICALS REVIEWS

a. Are all processes reviewed by line supervision and engineers, technology center, Safety Director and the LAD Reactive Chemicals Committee within approximately 90 days of a new superintendent or at scheduled Consolidated Audits, not to exceed two years?

Response(s): Yes, as schedules of the Audits allow.

b. Are appropriate process changes reviewed by the Reactive Chemicals Committee before they are installed; are pre-startup reviews held for process changes and recommissioning equipment; are pre-startup reviews held for appropriate processes that are infrequently operated (> 6 mos.)?

Response(s): Yes, per stated requirements and MOC. To insure adherence, many changes are reviewed with the Reactive Chemicals Committee and found to have no need for review. There are no set processes operated infrequently that have associated reactive chemical concerns requiring review. Non-routine processes are addressed via pre-startup reviews.

c. Are formulation changes reviewed by the Reactive Chemicals Committee before they are established?

Response(s): Formulation changes are rare to non-existent. If they were to occur, they would be reviewed per MOC.

NOT INCLUDED IN CONSOLIDATED AUDIT, BUT
MANDATORY FOR THE OTHER AUDITS:

CRITICAL INSTRUMENTS REVIEW
OPERATING DISCIPLINE REVIEW