

Process Safety Forum

The Process Safety Forum consists of representatives from UKPIA, TSA, CIA, OGUK and NIA

Process Safety Alert 003

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Process Safety Forum

Subject:

Hydrogen Fluoride (HF) Unit Water Mitigation Systems

Issue

The following is an extract from the CSB urgent recommendations following the release of HF at the CITGO Corpus Christi East Refinery in July 2009. The full text can be found by following the following link:

<http://idevmail.americaneagle.com/UserFiles/chemsafety/file/Urgent%20Recommendations%20to%20Citgo%20-%20Final%20Board%20Vote%20Copy.pdf>

1. On July 19, 2009 a hydrocarbon gas release occurred in the CITGO Corpus Christi East Refinery hydrogen fluoride (HF) alkylation unit at 1802 Nueces Bay Boulevard, Corpus Christi, Texas. The release ignited causing extensive damage; the ensuing fire burned for several days.
2. The fire critically injured one CITGO employee. One other employee was treated for possible HF exposure during emergency response activities.
3. The incident occurred when violent shaking in the process recycle piping broke two threaded connections, releasing highly flammable hydrocarbons. The shaking was caused by nearly complete flow blockage, which occurred due to the sudden failure of a control valve.
4. The control valve failed when an internal plug unthreaded from the valve stem, closing the valve. The only existing bypass valve was manually operated and became inaccessible following the hydrocarbon release.
5. The cloud of releasing hydrocarbons reached an adjacent unit and ignited. The ensuing fire caused multiple failures, releasing HF.
6. CITGO reported to the Texas Commission on Environmental Quality that approximately 21 tons (42,000 pounds) of HF released from alkylation unit piping and equipment, but was captured by the HF water mitigation system. CITGO reported 30 pounds of HF were not captured by the mitigation system.
7. While scientific studies have shown water mitigation systems to be an effective method of airborne HF removal, these studies indicate that the highest possible removal efficiency is 95 percent. The highest expected efficiency of field

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systems like the one used by CITGO is likely 90 percent or less. Based on a 90 percent efficiency, the atmospheric release from the alkylation unit would have been about 2 tons (4,000 pounds).

8. Prevailing winds during the incident carried any HF not captured by the water mitigation system toward the Corpus Christi ship channel and Nueces Bay.
9. CITGO installed the HF water mitigation system after a release and fire in the alkylation unit had resulted in an uncontrolled release of HF from the refinery in April 1997.
10. The CITGO Alkylation Unit Process Hazard Analysis, conducted in accordance with the OSHA Process Safety Management Standard for Highly Hazardous Chemicals (29 CFR 1910.119) and the EPA Chemical Accident Prevention Program (40 CFR 68), assumes that the HF mitigation system is available to minimize the consequences of an HF release.
11. During this incident, CITGO nearly exhausted its stored water supply for fire suppression and HF mitigation on the first day of the multi-day incident response. About 11.5 hours after the initial release, before the water supply was completely exhausted, the Refinery Terminal Fire Company began pumping salt water from the Corpus Christi ship channel into the CITGO fire water system using a barge equipped for firefighting. Multiple failures occurred during the salt water transfer, including multiple ruptures of the barge-to-shore transfer hoses and two water pump engine failures.
12. CITGO impounded the salt water used for HF mitigation and fire suppression on-site. Chemical analysis indicates salt water captured some of the released HF.
13. In the event of HF release the water mitigation system provides the last defence against an HF release into the surrounding community.
14. API Recommended Practice 751, *Safe Operation of Hydrofluoric Acid Alkylation Units*, recommends refineries audit the safety of HF alkylation operations every three years. API 751 details elements to be included as part of a comprehensive audit plan.
15. CITGO has never conducted a safety audit of HF alkylation operations at either of its US refineries equipped with HF alkylation units pursuant to recommendations of API Recommended Practice 751, *Safe Operation of Hydrofluoric Acid Alkylation Units*.
16. CITGO operates two US refineries with HF alkylation units, one in Corpus Christi, TX and one in Lemont, IL.

Learning

The following urgent recommendations were made by CSB to CITGO:

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1. Ensure adequate water supply to the CITGO HF mitigation system. Actions could include, but are not limited to, increasing onsite storage capacity, installing a permanent backup system, and developing procedures and training for water management in an emergency.
2. Complete a third-party audit of all (Corpus Christi, TX and Lemont, IL) CITGO HF alkylation unit operations in the United States as recommended by API Recommended Practice 751, *Safe Operation of Hydrofluoric Acid Alkylation Units*, Third Edition June 2007. The selected lead auditor shall have extensive knowledge of HF hazards, HF alkylation units, and API 751

Further Consideration None.

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