Risk Assessment in Chlorine Dioxide Systems

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Chlorine Dioxide
Chemical Pulp Mill Chlorine Dioxide System

- **Absorber**
- **Generator**
- **Storage**
- **Mixer**
- **Reaction Tower**
- **Washer**

Inputs:
- NaClO₃
- H₂SO₄
- Reductant
Mathieson and Solvay Processes

The diagram illustrates the processes involved in the production of chlorine dioxide (ClO₂) using the Mathieson and Solvay methods. The process begins with the input of sulfuric acid (H₂SO₄) and sodium chlorate (NaClO₃). These reactants are mixed and passed through a series of reactors, where chlorine dioxide (ClO₂) and air are produced. The ClO₂ and air mixture is then passed through a ClO₂ absorber where the desired product is separated. The remaining air and spent acid are handled appropriately.
Evolution of Bleaching Sequences

CHLORINE DIOXIDE REQUIREMENT IN VARIOUS BLEACH SEQUENCES

kg per ADt

CEHED  CEHDED  CEDED  DEDED

S1  S2

Typical Lowest and Highest
Illustration of Pulp Fibre
“Consistency”

Figure 1. Fiber network stability vs. consistency.
R3 or SVP Processes

Chlorine Dioxide Generation Systems
R8 and SVP-Lite Processes
Downflow Reaction Tower (1950)
Upflow Reaction Tower (1960)
J-Tube Upflow-Downflow (1970)
Chlorine Dioxide Solution Storage
Inherent Hazards of ClO$_2$

- Yellowish gas
- Boiling point of 11 °C
- Sweet odour similar to chlorine.
- Highly toxic.
  - IDLH level is 5 ppm in air
  - Prolonged exposure desensitizes people
  - Odour threshold is on the same order as its toxic limits.
Inherent Hazards (2)

- Highly unstable - may explode on heating, on exposure to sunlight or if subjected to shock or sparks.
- Strong oxidant –
  - reacts violently with combustible and reducing materials, such as organics, phosphorus, potassium hydroxide and sulphur
  - fire and explosion hazard
- Lower Explosive Limit is around 10% in air.
Inherent Hazards (3)

- At partial pressures above 120 mm Hg, it will decompose spontaneously and explode.
- At higher pressures the explosions become more violent; at 190 mm Hg explosion relief may be inadequate and rupture of the vessel may occur.
- These explosions can ignite combustible materials.
Inherent Hazards (4)

- Because it is unstable, ClO\(_2\) gas is generated on-site using one of the processes described earlier, and stored as a solution in water, typically at concentrations around 7-10 g ClO\(_2\)/L of water at 5C to 7C.
Inherent Hazards (5)

- In case of a spill of ClO₂ solution from storage or process lines, ClO₂ will start gassing off and form a toxic cloud.

- Molecular weight: 67.5.
  - heavier than air
  - will tend to result in heavy gas clouds that hug the ground and are relatively difficult to disperse.
Typical Storage System

- A typical storage system
  - Two (or more) cylindrical storage tanks in a containment dyke,
  - Associated pumping arrangement
  - Typical storage volumes: ~ 400 m$^3$ (100,000 US gal.) per tank.
Typical ClO₂ Storage System

- Dyke (capacity: 110% of largest tank)
- Pumphouse
- Pumps
- Suction line (at bottom)
- Overflow Sump
- Feed Lines
- Sweep Air Line
- Pad
- Stairs
- Buried
- To Closed Sewer
- To Scrubber

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Some Process Safety Aspects of Storage

- Fixed-roof tanks, generally made of FRP (fibreglass reinforced plastic) or are FRP-lined to guard against the corrosive solution
- Drainage and overflow to *acid* sewer
- Air sweep to keep concentration in air space in the tank below LEL
- Explosion hatches on tanks
- Vacuum breaks on tanks
Potential Process Safety Incidents

- Tank and pipe ruptures
  - Physical impact
  - Corrosion
  - Explosion in tank
  - Implosion of tank
Worst Case Scenario Modelling (1)

- Large spill overflowing dyke (three 60,000 USG tanks)
  - e.g., one suction line rupture, suction lines from other tanks not possible to isolate (no remote controlled valves)
  - Gassing off
    » pool of surface area equivalent to dyke area plus pool spread to 1 cm thickness
  - Distance (SLAB model) to IDLH of 5 ppm
    » 1800 m for D stability (neutral stability atmosphere, mechanical turbulence dominant) 5 m/s winds (medium winds)
    » 8100 m for F stability (very stable atmosphere, little turbulence) 1.5 m/s winds (low winds)
Worst Case Scenario Modelling (2)

- Large spill contained in dyke
  - e.g., one suction line rupture, suction lines from other tanks isolated by remote controlled valves
  - Gassing off from pool of surface area equivalent to dyke area minus tank footprints
  - Distance (SLAB model) to IDLH of 5 ppm
    » 120 m for D stability (neutral stability atmosphere, mechanical turbulence dominant) 5 m/s winds (medium winds)
    » 280 m for F stability (very stable atmosphere, little turbulence) 1.5 m/s winds (low winds)
Modelling Complications

- ClO₂ dissociates rapidly upon exposure to solar radiation (sunshine),
  - forms Cl₂ gas (for comparison, chlorine has an IDLH level of 10 ppm, double that of ClO₂).

- This natural dissociation will tend to reduce the hazard distances, and assuming “no dissociation” will result in conservative estimates of hazard zones.
Modelling Complications (2)

- Considering dissociation kinetics:
  - Under strong insolation conditions (bright sunshine at noon in July, southern Canadian latitudes)
    » assumption of complete conversion to Cl₂ would be justifiable
  - under clear skies shortly after sunrise in January
    » neglecting dissociation is more reasonable and justifiable
Risk Control Through Process Safety Management and Emergency Response

- Process safety management has many elements. E.g. (OSHA 29 CFR 1910.119):
  - employee participation,
  - process safety information,
  - process hazard analysis,
  - operating procedures,
  - training,
  - contractors,
  - pre-start safety reviews,
  - mechanical integrity,
  - work permit,
  - management of change,
  - incident investigation,
  - emergency planning and response, and
  - auditing.

- The risks associated with ClO₂ storage systems can be effectively controlled through judicious use of process safety management techniques including appropriate emergency response.
Typical Status of PSM in Pulp Mills

- Most pulp mills have many of these different elements in place, but not necessarily in a well-laid out program.
- The weakest elements are process hazard analysis and management of change.
- Regarding PHAs:
  - Engineering firms who design projects routinely carry out such studies,
  - This information is generally not passed on to the mills,
  - The mills themselves typically do not carry out such assessments on a periodic basis.
- This weakness manifests itself in management of change,
  - not all changes go through an appropriate level of PHA,
  - jeopardize future operational integrity of the mill processes.
Specific Risk Control Measures

- Add remote controlled valves next to the manual valves on the suction lines of storage tanks
  - Prevents necessity of an operator “swimming” to the manual valves for isolating storage tanks, in case of tank/line rupture.

- Install an alarm on high rate of level change (sound in the control room)
  - Improve response to tank/line rupture.
    » This arrangement became standard in BC mills following the risk assessments conducted in late 1990s.
    » Another arrangement is to install automatic valves and interlock them to a high rate of level change.

- Install foam systems for dykes, or covering a contained spill with tarp (tarpaulin)
  - Cut down gassing off thus reducing the size of the hazard zone.
Specific Risk Control Measures (2)

- Understand ahead of time where a spill could go within the complex sewer systems and interconnected buildings in pulp mills
  - Improve emergency response, and
  - Minimize damage to environmental systems and
  - Minimize potential for gassing off in unexpected locations thus preventing worker exposure.

- Think through ahead of time what to do with the waste in a contained spill
  - Improve the chances of painless recovery from a spill.
Specific Risk Control Measures (3)

- Implement a tank management program,
  - involves testing and inspection of tank shell thickness, nozzles, instrumentation,
  - regular log of this inspection and testing,
    » minimize chance of large tank breaches due to deterioration.

- Install detection for pipe rupture on long ClO₂ pipe runs (e.g., over 3000 ft) made of FRP,
  - Flowmeters on each end, interlock into shutdown in case of a larger-than-expected differential flowrate.
  - For start-up purposes, an interlock bypass may become necessary, which should be automatically deactivated after flow stabilization.
Specific Risk Control Measures (4)

- Fibreglass ClO₂ piping can experience problems with thermal shrinking and expansion, causing leaks.
  - Implement a rigorous preventive maintenance program to identify and correct such problems in a timely fashion.

- Drain valves on ClO₂ tanks are sometimes not locked, and could be inadvertently (or with malicious purpose) opened easily.
  - Install locks, or proxy switches that would alarm if a drain valve is open.

- Another common finding is open dyke drain valves, left open after a heavy rain.
  - Implement procedural controls and daily inspections to reduce this frequent cause of dyke breaches.
The most significant single PSM challenge in the chemical pulping sector of the pulp and paper industry is the chemical recovery boiler. But this risk has been so dramatic and so high profile, that is has been covered by the Black Liquor Recovery Boiler Advisory Committee, http://www.BLRBAC.org for over forty years.
**Closure (2)**

- Today, we have been talking about translating the same level of disciplined management to one of the next highest profile risks:
  - chlorine dioxide generation-absorption-storage systems which have made a tremendous evolution over 50-60 years.
  - bleaching tower designs that have evolved from downflow to upflow to J-tube to some high-intensity upflow.
  - dosage rates have risen from by a factor of six, 0.5% to 3.0%, and
  - production rates have risen by a factor of eight, from 250 ADt/day to 2000 ADt/day,
  - storage capacities have gone up by a factor of 45-50, just to sustain the same retention time.
Some of the industry’s most-publicized environmental emissions, with potential risks to the general public, have been the result of chlorine dioxide discharges from Canadian pulp mills over the past fifteen years.

In spite of the apparent superficial contravention of conventional wisdom regarding minimizing quantities stored,

- storage of chlorine dioxide solution in the quantities appropriate for competitive operation of kraft pulp mills can be achieved safely through observing basic process safety management discipline.