Tank explosion accident in the synthetic hydrochloric acid plant.

TOAGOSEI. CO.LTD  YOKOHAMA PLANT
HIDEAKI KURIHARA
Domestic business sites of TOAGOSEI
TOAGOSEI Yokohama & Kawasaki Plant

**Kawasaki Plant**
- PVC polymer
- ATBS monomer

**Yokohama Plant**
- Caustic soda
- Hydrochloric acid
- Sodium hypochlorite
- etc.
Famous place and food in Yokohama

- Yokohama chinatown
- Yokohama studium
- Cupnoodles Museum
- Minato Mirai 21 Area
- Iekei Ramen
* Products

1. Commodity
   Caustic soda, Liquefied chlorine, Hydrochloric acid, Sodium hypochlorite, Ferric chloride, Copper oxide, etc.

2. High-purity
   High-purity Liquefied hydrogen chloride, Hydrochloric acid, Caustic soda

* Scale

Site area: 97,000㎡
Building area: 19,000㎡
1. The situation of the explosion

- Date & Time: 2014/2/14 (Fri) 22:35
- Place: No.5 synthetic hydrochloric acid process yard
- Weather: Snow storm (22cm of snow at 23:00) → the heaviest snow in 28 years
  Temperature –0.1°C, Northern wind
  Maximum wind 17.9m/s
  (Yokohama Local Meteorological office)
- Influence: 3 HCl tanks were exploded and damaged
  (FRP4m³ × 2 + 8m³ × 1)
  Hydrochloric acid leaked and pollution water flowed

※Without human damage
  (There were 17 people in Yokohama Plant then.)
Process flow diagram of Hydrochloric acid

HCl Synthesis Tower

Tail gas Tower

HCl sol tank

Filter

Filtered tank

35% HCl

Pure water

Scrubber

Vent gas

Cl₂

H₂

Exploded part

Vent gas

Scrubber
2. The direct cause of the explosion

Gas composition in the vapor–phase part of a hydrochloric acid tank was included in explosive range. Therefore explosive gas had ignited by static electricity caused by snow and had exploded.
① Existence of a flammable material (H₂)

The hydrogen concentration of the vent gas was measured at 3 domestic TOAGOSEI plants. Amount of H₂ accompaniment from the hydrochloric acid synthetic tower was below.

<table>
<thead>
<tr>
<th>Plant</th>
<th>Amount of H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L/m³–35%HCL</td>
</tr>
<tr>
<td>Yokohama</td>
<td>4.7～8.7</td>
</tr>
<tr>
<td>Nagoya</td>
<td>18.7～22.7</td>
</tr>
<tr>
<td>Tokushima</td>
<td>3.1～49.6</td>
</tr>
</tbody>
</table>

＜Information outside the company＞

- A manufacturer of hydrochloric acid synthetic equipment had no recognition that hydrogen exists in a hydrochloric acid tank.
- There were also several cases of an explosive accident and explosive prevention by N₂ in a domestic other company. But, there are also a lot of companies which had no recognition that hydrogen exists in a hydrochloric acid tank.
Fluctuation of HCl sol tank level

The hydrochloric acid tank level was always repeating about 30% of fluctuation.
Simulation of the $\text{H}_2$ and $\text{O}_2$ concentration in the tank

Estimated result of $\text{H}_2$ concentration based on the fluctuation of the tank level

$\text{H}_2$ concentration of vapor-phase part of HCl tank

$\text{H}_2$ concentration (vol%)
The hydrogen concentration which is between 30% to 40% has the strongest Pe/Pi and the shortest time to attain max explosion pressure.

The HCl tank flew beyond the structure of HCl synthetic tower and reached the fall spot. The pressure of the tank probably rose in 0.85MPa and reached height 110m.
Ignition sources: Ignition by snow

Vent gas chimney
- Material: SUS 304
- Connected the grounding wire
- Drain pipes just below the chimney (PVC)

Hypothesis
- The chimney was filled with snow.
- The snow took on an electric charge by the snowstorm.
- Explosive gas was released by a rise of the tank level.

→ We guessed to have discharged electricity between the electric charged material (Snow) and the conductive material (Chimney) and had ignited.
Mr. specialist’s detonation Otsuka of National institute of occupational safety and health Japan guessed as follows. “The ignition point was the release side. Explosion changed into detonation on the way, and destroyed laying of the pipes to the tank dispersively. A diameter was that it expanded, and detonation in the tank had returned to an explosion”. 

No damage

Pipes were damaged → Explosion

Pipes were destroyed dispersively → Detonation
3. Recurrence prevention measure in equipment

The thought from which 2 inside 3 factors of combustion (flammables and combustion aids) are removed certainly. The countermeasure against static electricity is also put into effect.

<table>
<thead>
<tr>
<th>Measure</th>
<th>Contents</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂ purge of the tank</td>
<td>Supply more than pump capacity</td>
</tr>
<tr>
<td></td>
<td>Interlock system of the flow rate</td>
</tr>
<tr>
<td>Improvement of a vapor-liquid separation</td>
<td>Separator after the absorption tower</td>
</tr>
<tr>
<td>Stabilization of tank level control</td>
<td>Level Control by an inverter</td>
</tr>
<tr>
<td></td>
<td>PID optimization</td>
</tr>
<tr>
<td>Pressure indication of the tank</td>
<td>Pressure Indicator of the tank vapor phase</td>
</tr>
<tr>
<td></td>
<td>Interlock system of the pressure</td>
</tr>
<tr>
<td>Improvement of the material</td>
<td>Tank: FRP → SS+HRL</td>
</tr>
<tr>
<td></td>
<td>Pipe: PVC/FRP → PVC/Steel</td>
</tr>
<tr>
<td></td>
<td>Damaged prevention by snow falling</td>
</tr>
<tr>
<td>Connection the grounding wire</td>
<td>Tank, Vent gas pipe</td>
</tr>
<tr>
<td>Changing the shape of the chimney</td>
<td>Prevention blocked by snow</td>
</tr>
</tbody>
</table>
3. Recurrence prevention measure in equipment

- The shape of the chimney was changed
- Vent gas pipes: PVC/FRP → PVC/Steel
- FRP tank → SS-HRL, grounding wire
- N₂ gas supply
4. The effect by the measure

1) Result of the vent gas analysis after re-operation
   → H2: Less than 0.2% (Upper limit: 1.0%, Explosive minimum: 4.0%)

2) Fluctuation of the tank level
   → Fluctuation range: ±2%,
      A vapor-phase of the tank continues the positive pressure.
5. The essential cause and the measure

Why couldn’t the accident be stopped from happening?

→ “A bubble of H₂ from the synthetic tower is separated by U seal”
  wrong recognition
→ Insufficient in risk assessment at the plan stage
→ Measures of similar trouble at other plants wasn’t reflected.

〈Measures〉
① Key word “Contact of flammable gas and liquid”
  → Assumption and measure of H₂ bubble accompanying risk
② Level up of the risk assessment at the plan stage
③ Inspection of the accident and the trouble measure in the past