CHLORINE GAS V’s SODIUM HYPOCHLORITE

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ABSTRACT

Community and industrial concern regarding the potential health, environmental and safety risks associated with chlorine based disinfection has greatly increased over the past few years. The recent cryptosporidium scare in Sydney and the unprecedented political impact it has had on the Sydney Water Corporation has alerted the water industry to the potential consequences of any safety incident which can affect community health. Water boards have subsequently conducted risk assessments on all their operations concluding the “inherent risk” associated with the use of chlorine gas poses a potential safety concern.

Despite the outstanding safety record of the chlorine gas some water companies are considering converting their disinfection systems from chlorine gas to sodium hypochlorite due to the perceived safety benefit. The health risks associated with sodium hypochlorite, the increasing number of safety incidents occurring, the environmental damage from spills and the potential to greatly increase the cost of disinfection should be considered prior to conversion. This paper discusses the issues associated with the application of chlorine based disinfection products for water and waste water.

1.0 INTRODUCTION

Orica is the largest Australian manufacturer and investor in chlorine and it’s derivative products. Consequently, we believe it is our responsibility to set the market standard by operating to the highest ethical standards to ensure the safety of our customers, employees, the community and the environment.

Concern over the use of Chlorine disinfection is primarily due to environmental, regulatory and community perception of public risk. Public concern with acceptable levels of disinfection by-products has mounted pressure on government authorities to provide safe and “chemical free” potable water.

Orica firmly believes there is a requirement to provide chlorine and its derivatives as their use is application specific. In the case of chlorine based disinfection for water and waste water, Orica strongly believes that chlorine gas offers customers the lowest health risk for consumers, is the safest in use, and is the most cost effective and environmentally safe alternative. Sodium hypochlorite is becoming the largest contributor of safety incidents involving chlorine based disinfection.

Companies considering conversion to sodium hypochlorite should conduct an independent risk assessment of their sites to determine if there is a real safety risk. Companies who covert to sodium hypochlorite should fully investigate their suppliers to ensure that the product is fresh, has the required strength of available chlorine and is stored and transported in line with the strictest safety regulations. It is also strongly suggested that all chlorate levels are monitored in storage tanks and the receiving water.
2.0 SAFETY CONSIDERATIONS

The absence of fatalities in Australia related to the use of chlorine gas may be attributed to the rigorous safety practices (Hazop and Quantitative Risk Assessment) employed by manufacturers, distributors, regulators and customers of chlorine gas. The employment of these techniques to assess “inherent risk” (the potential to cause a fatality) has directly resulted in the dramatic reduction in “safety-in-use” incidents involving chlorine gas. Essentially, if you can forecast the potential risk of a chemical, you can eliminate safety incidents related to its use.

The minimisation of safety risks associated with the use of chlorine gas has been based on assessment of the “inherent risk” (the potential to cause a fatality) rather than measurement of “safety-in-use risk” (the number of safety incidents caused during the transport/storage/use of chlorine gas). The assessment method most commonly employed to assess “inherent risk” is the Quantitative Risk Assessment (QRA) which estimates the risk associated with the operation of a facility, calculates the likely frequency, and gauges the severity of an incident for a range of distances from the facility. The results are then used to take action to reduce risk (if required). Hazop studies are also conducted at the end of the process design stage to eliminate any unforeseen safety hazards. These techniques have successfully forecasted potential safety hazards. The reward for this rigorous application of risk assessment has been an outstanding safety record for manufacturers and users of chlorine gas ie negligible “safety-in-use” incidents.

The same rigorous risk assessment techniques have not been employed in ensuring the safe design, storage and transport of sodium hypochlorite. It appears that the reason for this oversight has been that sodium hypochlorite is considered as having an extremely low “inherent risk” and therefore, there has been little attention paid to “safety-in-use risk”. Whilst it is true that sodium hypochlorite is an inherently safer chemical, it does have the potential to create very dangerous safety hazards when stored, transported or used incorrectly. It is this perception regarding the relative safety of sodium hypochlorite which has directly resulted in an alarming increase in safety-in-use incidents involving sodium hypochlorite. Additionally, there are few regulatory guidelines in place to ensure the safe storage, transport and use of sodium hypochlorite. Subsequently, standard risk management practices have often not been conduct.

Orica has been compiling safety incident data on chlorine gas and sodium hypochlorite since 1996 via the Emergency Response System. A graph comparing sodium hypochlorite and chlorine gas incidents is shown below. The data shows an alarming increase in the number of sodium hypochlorite safety incidents occurring on customer sites. These incidents primarily involve:

- ground contamination from tank ruptures and valve leaks caused by poor maintenance/unsuitable materials of construction;
- pipe ruptures caused by hypo under pressure;
- burns/inhalations to operators due to lack of training in safe handling practices and failure to use appropriate Personal Protection Equipment (PPE);
- periods of non-disinfection due to absence of back-up supply on site.
Of most concern is the number of occurrences where sodium hypochlorite has been inadvertently mixed with acid creating an uncontrollable chlorine gas cloud. There have been far more incidents where members of the public have been exposed to chlorine gas in this way than via leaks from chlorine gas containers.

**Figure 2:**  *Chlorine vs Sodium Hypochlorite Safety Incidents*

**Categories**

A1. Plant manufacture

A2. Plant storage

A3. Plant container filling (includes cylinders/drums/bulk)

A4. Plant testing (includes degassing of containers)

B1. Transport - Customer delivery (includes bulk transfers or connection/disconnection of cylinders/drums)

B2. Transport - Loading / Unloading of containers onto truck

B3. Transport - In transit

C1. Customer storage

C2. Customer carrying out connection/disconnection of product packaging independently of Orica

C3. Customer process
3.0 HEALTH CONSIDERATIONS

Water Quality guidelines are becoming more stringent resulting in increased treatment and monitoring chemical. Additional to treatment costs is the enormous cost associated with public liability in the event of an incident involving public health (e.g., cryptosporidium). Chlorine gas can continually deliver the required level of disinfection when applied correctly, however there are serious doubts with regard to the use of sodium hypochlorite for disinfection of both potable water and waste water. These doubts have arisen for two reasons:

1. The degradation of sodium hypochlorite is virtually instantaneous. The resultant by-product, sodium chlorate, is dangerous to public health when it reaches defined levels. Consequently, countries such as USA have introduced water quality guidelines that prescribe the maximum allowable limit of chlorates in potable water. These limits may soon be implemented in the Australian Water Quality guidelines. These guidelines can be met if the sodium hypochlorite is used soon after manufacture, however, for any Water Company storing sodium hypochlorite on site, it is strongly recommended that they implement chlorate testing before the sodium hypochlorite is used to ensure that they do not breach the new guidelines. As the degradation process is strongly influenced by time and temperature, the storage time allowable for sodium hypochlorite will vary according to the customer’s storage conditions.

2. The degradation of sodium hypochlorite also affects the strength of the product. Orica manufactures hypochlorite each night for distribution the next day. Manufacture strength is typically 14 - 15% which ensures that the product is still at a minimum of 13% chlorine when it reaches our customers. However, depending upon temperature, storage conditions and storage time, the sodium hypochlorite will continue to lose strength. For customers storing hypochlorite on site, this may result in under-chlorination of the water supply due to the consequent loss in strength. For many companies this may create a situation equivalent to a period of non-disinfection and a serious health concern.

4.0 ENVIRONMENTAL CONSIDERATIONS

When considering the environmental risks of chlorine most people think of the dangers associated with the release of a chlorine cloud to the atmosphere. In reality a pure chlorine gas cloud will disperse very quickly and, according to the Chlorine Institute, is unlikely to reach/affect the Ozone layer. However, if chlorine is released in large quantities to the waterways, its strong oxidising properties will cause it to form by-products which are detrimental to marine plant and animal life. The likelihood of an accidental release of chlorine gas into the waterways is negligible, however, there is an increasing frequency of accidental releases of sodium hypochlorite into these sensitive environments. The most common causes of such leaks are transport accidents and tank ruptures.

The likelihood of a transport or storage incident increases with the number of deliveries and quantities stored. A single delivery of 6 x 920kg drums of chlorine gas would require the equivalent of 6 separate deliveries of 9,200L of sodium hypochlorite. Therefore, the number of transport and storage related incidents with sodium hypochlorite are higher.
Another significant reason why chlorine gas has very few transport or storage incidents is because it is transported and stored in specially engineered containers which are strong enough to withstand a fall from a multistory building.

Sodium hypochlorite is still chlorine but in a liquid form, it has the same ability to negatively impact the environment, however, because it is perceived to be “safe” regulations do not specify the same safeguards for transport, storage and use. This is a dangerous oversight which must be rectified if sodium hypochlorite is to safely replace chlorine gas in water disinfection.

5.0 COST CONSIDERATIONS

An objective summary of the key capital, maintenance and chemical costs and availability issues for chlorine gas and sodium hypochlorite are tabulated below.

**Table 1: Capital, Equipment & Maintenance Costs**

<table>
<thead>
<tr>
<th></th>
<th>Chlorine Gas</th>
<th>Sodium Hypochlorite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost of large facilities</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Redundancy</td>
<td>Easily built in</td>
<td>Costly</td>
</tr>
<tr>
<td>Ease of Storage</td>
<td>Easy to store</td>
<td>Degrades over time</td>
</tr>
<tr>
<td>Maintenance</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Inspection/testing freq.</td>
<td>Regular</td>
<td>Regular</td>
</tr>
<tr>
<td>Equipment life</td>
<td>Long life (&gt; 15 years)</td>
<td>Short to medium tank life (&lt; 5-10 years)</td>
</tr>
<tr>
<td>System adaptability</td>
<td>Can be used for complex systems</td>
<td>Used in simple systems</td>
</tr>
</tbody>
</table>

**Table 2: Chemical Cost**

<table>
<thead>
<tr>
<th></th>
<th>Chlorine Gas</th>
<th>Sodium Hypochlorite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Available Chlorine (%)</td>
<td>100% Pure chemical</td>
<td>12.5% w/v Diluted unstable chemical</td>
</tr>
<tr>
<td>Transport Costs</td>
<td>Lower</td>
<td>Higher</td>
</tr>
<tr>
<td>Suitability for remote sites</td>
<td>Suitable</td>
<td>Expensive</td>
</tr>
<tr>
<td>Chemical Cost variability with volume</td>
<td>Cost decreases relatively as usage increases</td>
<td>Costs increases relatively as usage increases</td>
</tr>
<tr>
<td>Bulk Availability</td>
<td>Readily available Road tankers, drums &amp; cylinders</td>
<td>Product availability limited for very large facilities</td>
</tr>
</tbody>
</table>

**Table 3: Availability**

<table>
<thead>
<tr>
<th></th>
<th>Chlorine Gas</th>
<th>Sodium Hypochlorite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Availability</td>
<td>Readily available</td>
<td>Available</td>
</tr>
<tr>
<td>Storage</td>
<td>May store for long periods</td>
<td>Limited storage due to decomposition</td>
</tr>
<tr>
<td>Quality</td>
<td>Consistent &amp; high</td>
<td>Quality ex factory only</td>
</tr>
<tr>
<td>Storage Depots</td>
<td>Storage depots across the country</td>
<td>No storage depots</td>
</tr>
<tr>
<td>Seasonal Demand</td>
<td>High demand in summer</td>
<td>High demand in summer</td>
</tr>
<tr>
<td>Stock Management</td>
<td>Stock management is easy</td>
<td>Stock management is</td>
</tr>
</tbody>
</table>
Contrary to chlorine gas, limited consideration is given to safety systems and secondary back up (required to ensure the same functionality and level of redundancy) when determining the costs associated with the use of sodium hypochlorite. Consequently, the customer is often led to believe that the sodium hypochlorite installation is significantly cheaper. In reality, the opposite is true.

A sodium hypochlorite installation which is correctly designed to provide the same level of operator safety and reliability as a chlorine gas installation may cost up to four times that of the chlorine gas installation. Additionally, the chemical cost of sodium hypochlorite is historically greater than that of chlorine gas. Essentially, the triple double line associated with chlorine gas is invariably better than that of sodium hypochlorite.