Hypochlorite Production
General Information

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Cinderella
Powell Fabrication & Mfg.

- Sodium hypochlorite production equipment starting in 1964 with filtration since 1983
- 75% of NaOCl in US made on Powell equipment
- 90% in Canada
- Significant production in other countries – Brazil, 80% Mexico, 80% Chile, Taiwan, Philippines, 65% Costa Rica, Saudi Arabia and others
- Chlorine scrubbing and chlorine valve emergency shutoff systems
- Chemical Blending Systems: NaOCl, Caustic, HCl, sulfuric, methanol, ammonia, etc.
- One Shop Point: Engineering, Procurement, Fabrication, Startup, Field Services
Bleach Plant Owners
Powell Equipment Owners
Discussion Topics

- Sodium Hypochlorite Chemistry
- Packed Tower Chemistry
- Oxidation Reduction Potential (ORP/Redox)
- Batch to Continuous Chlorine Scrubbing
- Batch to Continuous Sodium Hypochlorite Production
- Filtration & Hypo Dilution Systems
Terms of Hypochlorite Strength

- Grams per Liter of Available Chlorine
- Grams per Liter of Sodium Hypochlorite
- Trade Percent of Available Chlorine
- Weight Percent of Available Chlorine
- Weight Percent of Sodium Hypochlorite
Production of Sodium Hypochlorite

- \( \text{Cl}_2 + 2 \text{NaOH} = \text{NaOCl} + \text{NaCl} + \text{H}_2\text{O} \)
- Exothermic reaction
- 526 BTU/Pound of chlorine if \( \text{Cl}_2 \) liquid
- 626 BTU/Pound of chlorine if \( \text{Cl}_2 \) vapor
- Slight amount of excess NaOH always remains in solution (typically 3-5 GPL or 0.25% to 0.35% by weight)
- pH for commercial NaOCl (typically greater than 13)
Basis of Production

• 32% or 50% sodium hydroxide is diluted to 17% NaOH for typical commercial strength NaOCl
• Heat of solution removed
• Cl₂ added into solution until excess caustic is reduced to the 3-5 GPL excess caustic range – approximately 13 pH
• Cl₂ addition should always be controlled by ORP (oxidation reduction potential)
• Process can be either batch or continuous
Sodium Hypochlorite Decomposition

- Parameters That Influence Decomposition
  - Concentration
  - Temperature
  - Ionic Strength
  - Transition Metal Ions

- 2\textsuperscript{nd} Order Rate = k_2 [OCl\textsuperscript{-}]^2

- Primary Pathway
  - OCl\textsuperscript{-} + OCl\textsuperscript{-} → ClO\textsubscript{2}\textsuperscript{-} + Cl\textsuperscript{-}
  - OCl\textsuperscript{-} + ClO\textsubscript{2}\textsuperscript{-} → ClO\textsubscript{3}\textsuperscript{-} + Cl\textsuperscript{-}

- Stoichiometry
  - 3OCl\textsuperscript{-} → ClO\textsubscript{3}\textsuperscript{-} + 2Cl\textsuperscript{-}

- Secondary Pathway
  - OCl\textsuperscript{-} + OCl\textsuperscript{-} → O\textsubscript{2} + 2Cl\textsuperscript{-}
  - “uncatalyzed” and “catalyzed”
Unwanted By-Products

- **Bromate** (BrO$_3^-$)
  - Bromide ion in salt used to make Cl$_2$
  - Forms Br$_2$ (Impurity in caustic)
  - Reacts with caustic to form (BrO$_3^-$)

- **Chlorate** (ClO$_3^-$)
  - Inefficiency of chlorine/caustic reaction
  - 3 OCl$^-$ → ClO$_3^-$ + 2 Cl$^-$

- **Perchlorate** (ClO$_4^-$)
  - Decomposition of Chlorate Ion
  - OCl$^-$ + ClO$_3^-$ → ClO$_4^-$ + Cl$^-$
Hypochlorite Production

- Hypochlorite Productions
  - Tower System
  - Batch vs. Continuous
  - ORP Control
Initial Tower Cl₂ & NaOH Reaction

- Cl₂ + 2NaOH = NaOCl + NaCl + H₂O
- 17 - 20% NaOH typical scrubbing solution strength
- High pH reaction >11
Tower Reaction Zones End of Batch

- Top of tower – High pH (NaOH – NaOCl – NaCl)
- Center of tower – pH > 11 (NaOH – NaOCl - NaClO3 - Cl2)
- Bottom of Tower-Low pH (NaOCl – NaClO3 – NaCl – Cl2)
Ending Batch Reactions

- $\text{Cl}_2 + \text{NaOCl} + \text{H}_2\text{O} = 2\text{HOCl} + \text{NaCl}$
- $2\text{HOCl} + \text{NaOCl} = \text{NaClO}_3 + 2\text{HCl}$
- End reaction is: $3 \text{NaOCl} = \text{NaClO}_3 + 2 \text{NaCl}$
- Occurs in low pH regions at bottom of tower
Packed Tower Advantages

- Very good chlorine reactor
- Low gas pressure drop
- High inert gas loading
- Predictable results
- Low PPM chlorine outlet concentrations
Packed Tower Disadvantages

- Packed towers - Poor NaOCl production units.
- Low excess caustic less than 2% - 3% by weight produces high NaClO3
- NaOCl side reaction to NaClO3 creates more salt, potentially plugging the tower packing.
- Each 1 gpl of NaClO3 loses 2.1 GPL of NaOCl
- Packed towers are limited in strength of NaOCl due to NaClO3 side reactions creating NaCl and high excess caustic
Production Losses

- Typical packed towers produce 135-155 gpl NaOCl with 12-15 gpl excess NaOH and 8-10 gpl NaClO₃
- High quality hypo is 135 -155 gpl NaOCl, 3 gpl excess NaOH and 1.0 gpl NaClO₃
- 25,000 MT of hypo per year of high quality hypo versus packed tower hypo equals a savings of 305 tons of Cl₂ and 532 tons of NaOH @ 135 gpl
Production Improvements

- Convert batch towers to continuous
- Operate towers at higher excess caustic such as 3-4% excess NaOH or greater
- Move hypo production downstream of chlorine towers
- Allows use of cooling tower water in lieu of chilled water for towers and hypo production
Production Improvements

- Allows production of up to 16.5% by weight (200 gpl available chlorine)
- Reduce Excess NaOH to as low as 2-3 gpl
- Reduce NaClO3 to as low as 1 gpl
- Reduce Operator Labor (elimination of 1 or more operators per shift)
- Reduce Shipping Cost
ORP Instrumentation

- ORP for chlorine scrubbers and hypo production
- Successful patented electrodes developed by Dow in 1960’s
- Originally sold under license by Powell since 1963
- Voltage increases as sodium hydroxide decreases
ORP Control

Graph: ORP vs wt% NaOH
Tower Design Changes

- Add ORP electrodes, indication and alarms
- Location of electrodes depend on process design
- Convert from batch towers to continuous system
- Requires level control and ORP control for automatic caustic addition
Hypochlorite Prod. Downstream of Towers

- Towers are continuous
- Towers operate at high excess NaOH levels
- Towers have low NaClO3
- No chilled water
- Safer operation
Advantages

- Continuous Equipment to chlorinate tower hypo
- Uses scrubber solution from 3-4% excess NaOH and higher to maximum of 21% caustic
- Liquid and/or gas (wet or dry) chlorine for final chlorination
- Cooling Tower Water during production
- Chilled water used for some storage applications
Additional Advantages

- Hypo production during cell room maintenance if liquid chlorine is used
- Reduced shipping costs due to higher strength
- High turn down of production such as 250 ton/day down to 25 ton per day
- Totally automatic with extremely good repeatability of bleach strength and excess caustic
## Typical Real Case

### 100 Ton per day Bleach Unit

<table>
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<tr>
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<th>Junio 27/03 al Oct 10/03</th>
<th>Oct 08/03 al Dic 9/03</th>
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<tbody>
<tr>
<td>Número de Datos</td>
<td>201</td>
<td>189</td>
</tr>
<tr>
<td>NaOCl</td>
<td>146.031</td>
<td>146.241</td>
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<tr>
<td>NaCl</td>
<td>145.649</td>
<td>128.729</td>
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<tr>
<td>NaCl Teórico</td>
<td>114.640</td>
<td>114.810</td>
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<tr>
<td>Sobrante NaCl</td>
<td>31.01</td>
<td>13.92</td>
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</table>
Typical Real Case

- Difference 16.92 gr Salt/lt bleach
- Equivalent to 32.33 gr bleach/lt
- 100 ton per day bleach production means over consumption 2.57 ton chlorine and 2.9 ton dry caustic
Next Generation Hypochlorite Production

Powell HSLS Hypo Process Diagram
HSLS Hypo Solution
## Traditional Hypo vs. HSLS Hypo

<table>
<thead>
<tr>
<th>Tradition Hypo</th>
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<tbody>
<tr>
<td><strong>NaOCl</strong></td>
<td><strong>NaCl</strong></td>
</tr>
<tr>
<td>Wt. %</td>
<td>Wt. %</td>
</tr>
<tr>
<td>30.0%</td>
<td>X</td>
</tr>
<tr>
<td>25.0%</td>
<td>X</td>
</tr>
<tr>
<td>20.0%</td>
<td>X</td>
</tr>
<tr>
<td>16.5%</td>
<td>13.0%</td>
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<tr>
<td>15.0%</td>
<td>11.9%</td>
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<tr>
<td>13.0%</td>
<td>10.4%</td>
</tr>
<tr>
<td>10.5%</td>
<td>8.3%</td>
</tr>
<tr>
<td>8.0%</td>
<td>6.3%</td>
</tr>
<tr>
<td>6.0%</td>
<td>4.7%</td>
</tr>
<tr>
<td>3.0%</td>
<td>2.4%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>HSLS Hypo</th>
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</tr>
</thead>
<tbody>
<tr>
<td><strong>NaOCl</strong></td>
<td><strong>NaCl</strong></td>
</tr>
<tr>
<td>Wt. %</td>
<td>Wt. %</td>
</tr>
<tr>
<td>30.0%</td>
<td>8.5%</td>
</tr>
<tr>
<td>25.0%</td>
<td>7.1%</td>
</tr>
<tr>
<td>20.0%</td>
<td>5.7%</td>
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<tr>
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<td>2.3%</td>
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<tr>
<td>6.0%</td>
<td>1.7%</td>
</tr>
<tr>
<td>3.0%</td>
<td>0.9%</td>
</tr>
</tbody>
</table>
Chemistry Advantages

- Reduction in ionic strength of the solution:
  - Slower decomposition resulting in a longer half-life
  - Less chlorate ion formation
  - Less perchlorate ion formation
  - Less oxygen formation
Chlorate Formation

Diluted HSLS Hypo vs. Traditional Hypo @ 90°F

- Strength, wt. % NaOCl vs. Sodium Chlorate, GPL
- Days vs. Sodium Chlorate, GPL
- Graph showing comparison of Diluted HSLS Hypo and Traditional Hypo over 30 days.
What are the Production Advantages?

- Reduced chlorine and caustic consumption per liter produced
- Recovery of salt for raw material savings
- Improved stability and reduced weight allow more flexibility of logistics
  - Lower specific gravity will reduced the overall weight load for shipment of same volume
  - Increased volume per shipment for same load weight
Salt Savings for HSLS Hypo

- Approximately 1,650-1,815 kg. of NaCl consumed to produce 1,000 kg. of chlorine
- 1,000 kgs. of chlorine reacted to 30% NaOCl = 615 kg. of NaCl savings by reclaiming salt
- 615 kg of reclaimed salt = 34-37% needed for original electrolysis
- Reclaimed salt is very pure; if returned back to chlor-alkali plant only requires secondary brine treatment
## Salt Purity

<table>
<thead>
<tr>
<th>Element / Compound</th>
<th>mg/kg</th>
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<tbody>
<tr>
<td>NaCl</td>
<td>99.85%</td>
</tr>
<tr>
<td>Moisture</td>
<td>3.85%</td>
</tr>
<tr>
<td>Insolubles</td>
<td>&lt;0.005%</td>
</tr>
<tr>
<td>Al</td>
<td>&lt;1.6</td>
</tr>
<tr>
<td>Ba</td>
<td>&lt;0.17</td>
</tr>
<tr>
<td>Ca</td>
<td>0.39</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Sr</td>
<td>&lt;1.6</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.67</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>N/D</td>
</tr>
</tbody>
</table>
HSLS Hypo Shipping Advantages

- HSLS Hypo is stored on producers site at 10°C.
- 19 M3. tank truck load of 30% wt. equals 52 M3 of 13% wt.
- High dilution ratio allows for shipment flexibility.
  - Shipment of 30% wt.
    - Economically ship 2.75 time farther
    - Increase total delivered volume by 2.75, diluted at distribution center or customer site
  - Shipment of diluted product
    - Increased stability allows for decreased shipping strength
- One tank truck load (10 M3) of 13.0% diluted HSLS Hypo contains 1,800 kg. less salt than tradition hypo.
HSLS Hypo Shipping
HSLS Hypo Shipping
HSLS Hypo Summary

- HSLS Hypo with lower salt concentration offers a product that is more stable and lighter.
  - Greater stability means less sodium chlorate and perchlorate formation during decomposition.
- Reclaim salt to improve chlor-alkali plant efficiencies.
- HSLS Hypo can improve the shipment economics by:
  - Increasing shipping radius from the plant
  - Lighter product therefore more hypo per load
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