Polyvinyl Chloride
• Review Chlorine and Vinyl Chloride Monomer (VCM) Process Technologies
• Provide Overview Of Polyvinyl Chloride (PVC) Process
• Identify VCM Safe Handling Practices
• Explore Equipment Design Examples From PVC Processes
Chlorine
Siemens
Caustic - Chlorine Process

Markel Eclipse Membranes Brochure
Salt Dome To Electrolytic Cell

- BRINE STORAGE
- ELECTROLYTIC CELL
- BRINE PURIFICATION

- Cap Rock
- Gas
- Water
- Oil
- Salt
- Rock Salt
- Pumphouse
- River
Chlorovinyls

Steam Requirements

Natural Gas Purchased

COGEN FACILITY

ELECTRICITY

SALT DOME

BRINE

CHLORALKALI

CHLORINE

VCM

VINYL RESINS

VINYL COMPOUNDS

Chlorine

Ethylene
Electrolytic Cell Technology

- Mercury
- Diaphragm
- Membrane
Mercury Electrolytic Cell

Chlorine and Sodium Hydroxide, Kirk-Othmer 4 Ed.
Inlet Streams
6 – Water
10 – Brine (1 = Brine Level)

Components
2 – Metal Anodes
3 – Mercury Cathodes
4 – Mercury Circulating Pump
5 – Decomposer
7 – Graphite Packing

Outlet Streams
8 – Caustic Liquor
9 – Mercury
11 – Brine
12 – Hydrogen
14 – Chlorine (13 = Chlorine Vapor)
15 – Wash Water

Chlorine and Sodium Hydroxide, Kirk-Othmer 4 Ed.
Chlorine and Sodium Hydroxide, Kirk-Othmer 4 Ed.
Diaphragm Electrolytic Cell

Production Chlor-Alkali – Best Available Techniques, JRC 2014
Diamond MDC Type
Diaphragm Electrolytic Cell

Hooker H Type

Chlorine and Sodium Hydroxide, Kirk-Othmer 4 Ed.
Diaphragm Cell Row

Occidental
• **Diaphragm**
  – Originally Asbestos
  – Tephram (Non-Asbestos)
  – Polyaramix (Non-Asbestos)
  – Life: 200 to 400 Days

• **Anode Electrodes**
  – Coated Titanium
  – 8 to 15 Years

• **Cathode Electrodes**
  – Carbon Steel
  – 5 to 15 Years
Chlorine and Sodium Hydroxide, Kirk-Othmer 4 Ed.
Membrane Electrolytic Cell

Chlorine and Sodium Hydroxide, Kirk-Othmer 4 Ed.
Chlorine and Sodium Hydroxide, Kirk-Othmer 4 Ed.

Ford, Bacon & Davis, LLC
<table>
<thead>
<tr>
<th>Component</th>
<th>Diaphragm Cell</th>
<th>Mercury Cell</th>
<th>Membrane Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>Steel/steel coating with nickel</td>
<td>Mercury flowing over steel</td>
<td>Steel or nickel with a nickel-based coating</td>
</tr>
<tr>
<td>Anode</td>
<td>Titanium with ruthenium and titanium oxide coatings; iridium oxide added to improve performance and extend life</td>
<td>Titanium with ruthenium and titanium oxide coatings; iridium oxide added to improve performance and extend life</td>
<td>Titanium with ruthenium and titanium oxide coatings; iridium oxide added to improve performance and extend life</td>
</tr>
<tr>
<td>Diaphragm/ Membrane Material</td>
<td>Asbestos and fibrous polytetrafluoroethylene</td>
<td>None</td>
<td>Ion-exchange membrane (fluorinated polymers)</td>
</tr>
<tr>
<td>Cathode Product</td>
<td>10 to 15% sodium hydroxide solution, containing 15 to 17% salt (NaCl) (sent to evaporator for further processing); hydrogen gas</td>
<td>Sodium amalgam (sent for further processing through a decomposer cell)</td>
<td>30-33% sodium hydroxide solution (sent to evaporator for further processing); hydrogen gas</td>
</tr>
<tr>
<td>Anode Product</td>
<td>Chlorine gas containing some oxygen, salt, water vapor, and sodium hydroxide</td>
<td>Chlorine gas containing some oxygen, salt, and water vapor</td>
<td>Chlorine gas containing some oxygen, salt, and water vapor</td>
</tr>
<tr>
<td>Evaporator/Decomposition Product</td>
<td>50% sodium hydroxide solution containing 1% salt; solids salt from evaporator</td>
<td>50% sodium hydroxide solution; hydrogen gas</td>
<td>50% sodium hydroxide solution with very little salt</td>
</tr>
<tr>
<td>Electricity Consumption</td>
<td>2,550 to 2,900 kWh/ton chlorine gas</td>
<td>3,250 to 3,460 kWh/ton chlorine gas</td>
<td>2,530 to 2,600 kWh/ton chlorine gas</td>
</tr>
</tbody>
</table>

## Cell Technology Comparison

<table>
<thead>
<tr>
<th></th>
<th>Mercury cell</th>
<th>Diaphragm cell</th>
<th>Membrane cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell voltage /V</td>
<td>-4.4</td>
<td>-3.45</td>
<td>-2.95</td>
</tr>
<tr>
<td>Current density / A cm(^{-2})</td>
<td>1.0</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Current efficiency for Cl(_2)/%</td>
<td>97</td>
<td>96</td>
<td>98.5</td>
</tr>
<tr>
<td>Energy consumption / kWh per ton of NaOH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Electrolysis only</td>
<td>3150</td>
<td>2550</td>
<td>2400</td>
</tr>
<tr>
<td>(b) Electrolysis + evaporation to 50% NaOH</td>
<td>3150</td>
<td>3260</td>
<td>2520</td>
</tr>
<tr>
<td>Purity Cl(_2)/%</td>
<td>99.2</td>
<td>98</td>
<td>99.3</td>
</tr>
<tr>
<td>Purity H(_2)/%</td>
<td>99.9</td>
<td>99.9</td>
<td>99.9</td>
</tr>
<tr>
<td>O(_2) in Cl(_2)/%</td>
<td>0.1</td>
<td>1-2</td>
<td>0.3</td>
</tr>
<tr>
<td>Cl(^-) in 50% NaOH/%</td>
<td>0.003</td>
<td>1-1.2</td>
<td>0.005</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>concentration prior to evaporation/%</td>
<td>50</td>
<td>12</td>
<td>35</td>
</tr>
<tr>
<td>Mercury pollution considerations</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Requirement for brine purification</td>
<td>Some</td>
<td>More stringent</td>
<td>Very extensive</td>
</tr>
<tr>
<td>Production rate per single cell / tons</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH per year</td>
<td>5000</td>
<td>1000</td>
<td>100</td>
</tr>
<tr>
<td>Land area for plant of 10(^5) tons</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH per year / m(^2)</td>
<td>3000</td>
<td>5300</td>
<td>2700</td>
</tr>
</tbody>
</table>

**Teknik Elektrokimia**
Cell Power Distribution (1500 TPD Cl₂)

- **TOTAL CELL VOLTAGE:** 101*3.5 V = 353.5 V
- **OTHER VOLTAGE DROPS:** 16.5 V
- **TOTAL VOLTAGE DROP:** 370 V

- **CELL POWER REQUIREMENT = 170 MW**  84%
- **OTHER POWER REQUIREMENT = 32 MW**  16%
- **TOTAL POWER REQUIREMENT = 202 MW**  100%

- **150 kA @ 370 V DC**
  - LINE 1
  - LINE 2
  - LINE 3

- **HIGH VOLTAGE AC**
  - 303*150 kA*0.95 = 43,202 kA

- **LOW VOLTAGE DC**
  - 150 kA @ 370 V DC
BRINE GENERATION (SALT DOME) → RAW BRINE HEATING/REACTION → BRINE CLARIFICATION → CLARIFIED BRINE TO PREHEATING

BRINE CLARIFICATION ↓

UNDERFLOW FILTRATION → RECYCLE WATER

CLARIFIED BRINE TO PREHEATING

RECYCLE WATER → BRINE HEATING/REACTION

SOLIDS TO DISPOSAL
HOT WET CHLORINE FROM ELECTROLYTIC CELLS

CHLORINE COOLING

CONDENSATE STRIPPING

STRIPPED CONDENSATE RECYCLE TO BRINE

98% SULFURIC ACID

SPENT SULFURIC ACID TO UTILITIES

CHLORINE DRYING

CHLORINE COMPRESSION

TAIL GAS TREATMENT

VENT TO ATMOSPHERE

LIQUID CHLORINE FOR COOLING

CHLORINE LIQUEFACTION

LIQUID CHLORINE TO STORAGE

Ford, Bacon & Davis, LLC
CAUSTIC EVAPORATION

EVAPORATED WATER

WEAK CELL LIQUOR FROM ELECTROLYTIC CELLS

CONCENTRATED CAUSTIC

SALT REMOVAL

RECYCLE SALT TO BRINE SATURATOR

CAUSTIC PRODUCT TO STORAGE
Vinyl Chloride Monomer (VCM)
Vinnolit VCM Process
Vinnolit VCM Process
Vinnolit VCM Process
Vinnolit VCM Process
Polyvinyl Chloride (PVC)
Vinyl Chloride (VCM) + Organic Peroxide Initiator → Poly Vinyl Chloride (PVC)
• **Thermosetting**
  – Cross-Linking During Curing
  – High Temperature Applications
  – Polyurethane, Polyester, Vinyl Ester, Epoxy

• **Thermoplastic**
  – No Cross-Linking During Curing
  – Recyclable / Remoldable
  – Polyethylene, Polypropylene, PVC
• **Suspension**
  – > 80% Market
  – Multiple Purposes (Pipe, Building Materials, Medical Products)

• **Emulsion**
  – < 10% Market
  – Very Small Particle Size (Latex)
  – PVC Coatings

• **Bulk / Mass**
  – < 5% Market
  – Hard Plastic Sheets/Bottles
• In Water Suspension
• Exothermic / Organic Peroxide Initiator
• Multiple Recipes
  – Pipe Grade
  – Film Grade
• Batch Reaction
  – Reactors Clustered In Trains
  – Transition From Batch To Continuous Operation
• VCM Recovery And Reuse
  – 90% Conversion
  – Minimize VCM Losses
<table>
<thead>
<tr>
<th>Reactor Step</th>
<th>Minutes</th>
<th>Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge / Heat Up</td>
<td>45</td>
<td>0.75</td>
</tr>
<tr>
<td>Reaction</td>
<td>165</td>
<td>2.67</td>
</tr>
<tr>
<td>Pressure Drop</td>
<td>30</td>
<td>0.50</td>
</tr>
<tr>
<td>Blowdown / Recovery / Wash</td>
<td>60</td>
<td>1.00</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>300</td>
<td>5.00</td>
</tr>
</tbody>
</table>
DISSOLVING

DEMINERALIZED WATER

DISPERSANT

VINYL CHLORIDE

RECOVERED VINYL CHLORIDE

INITIATOR

REACTOR

AIR EVACUATION

VCM RECOVERY

PVC SLURRY
DEMINERALIZED WATER

DISPERSANT

VINYL CHLORIDE

RECOVERED VINYL CHLORIDE

INITIATOR

AIR EVACUATION

VCM RECOVERY

REACTOR

PVC SLURRY
- Particle Size Control
- Uniform Particle Size Distribution
- Particle Porosity
DEMINERALIZED WATER

DISPERASNT

VINYL CHLORIDE

RECOVERED VINYL CHLORIDE

INITIATOR

AIR EVACUATION

VCM RECOVERY

REACTOR

PVC SLURRY
### Increasing PVC Production

<table>
<thead>
<tr>
<th>Change</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Size</td>
<td>Larger Batches</td>
</tr>
<tr>
<td>Closed Mode Operation</td>
<td>Minimize Reactor Openings / Process Steps</td>
</tr>
<tr>
<td>External VCM Removal</td>
<td>Reduce Reactor Cycle Time / Continuous Slurry Stripping</td>
</tr>
<tr>
<td>Preheating Demin Water</td>
<td>Reduce Reactor Cycle Time</td>
</tr>
<tr>
<td>Clean Wall Technology</td>
<td>Reduce Reactor Cleaning Frequency / Increase Uptime</td>
</tr>
</tbody>
</table>
Reaction Heat Transfer Vs Time

Total Reaction Heat Removal:

28.7 MM Btu/hr
Chilled Water To Reactor Vs Reaction Time

Chilled Water Flow Rate (gpm) vs Time (Minutes)

Ford, Bacon & Davis, LLC
Ford, Bacon & Davis, LLC
Conventional Reactor

High-Performance Reactor

A Cooling channel
B Cladded steel wall
C PVC-suspension
D Half-pipe wall
E Cooling coil

Suspension

Ford, Bacon & Davis, LLC
Pfaudler RCI Agitator Impeller

- Radial Design
- High Shear (Low Efficiency)
- Poor Pumping
- Long History With PVC Reactors
Slurry Stripping

- PVC Slurry from Reactors
- Stripped Slurry to Drying
- Vent to VCM Recovery
- Stripped Slurry in the Feed Tank
- Feed – Bottoms Exchanger
- Steam
- Slurry Stripper

Ford, Bacon & Davis, LLC
56
Baffle Trays

- Low Pressure Drop
- Low Fouling
- Low Efficiency
Spiral Heat Exchanger
VCM Recovery

VCM FROM TRAIN 1

VCM FROM TRAIN 2

VCM FROM TRAIN 3

VCM COMPRESSORS

VCM VENT CONDENSERS

RVCM TO REACTORS

VENT GAS TO INCINERATION

RECOVERED VCM STORAGE VESSEL
Liquid Ring Compressors

Gardner Denver Nash
Gardner Denver Nash
Wet-Seal Gas Holder

Variable Volume Gas Container / Gasometer

Gas

Water

Gas In

Gas Out
Dry-Seal Gas Holder
PVC SLURRY FROM STRIPPER

PVC SLURRY TANK

CENTRIFUGE FEED PUMP

DECANTING CENTRIFUGE

WATER TO TREATMENT

PVC WET CAKE TO DRYER

Ford, Bacon & Davis, LLC
Decanting Centrifuge

1. VIBRATION ABSORBER  5. CONVEYOR  9. BEARING SEAT
2. BASE  6. BOWL  10. GEARBOX
3. MAIN MOTOR  7. SCREEN  11. LIQUIDS DISCHARGE
4. FEED TUBE  8. COVER  12. SOLIDS DISCHARGE
Air Heater

Ford, Bacon & Davis, LLC
Cyclones

Low Efficiency (less air flow, no vortex finder)

1929 Prockat
1939 Shepherd & Lapple
1949 ter Linden (scroll inlet)
1951 Stairmand
1965 Peterson & Whitby
1969 Swift
1976 Avant, Parnell & Sorenson
Rotex

Incoming Material

Fines
- 2.1%
- 97.9%

Product
- 3%
- 95.0%

Overs
- 3.6%
- 96.4%
Flex-Kleen Model CT
Pressure Blower Package

- Inlet Silencer
- Inlet Air Filter
- Blower
- Belt Drive With Guard
- Outlet Silencer
- Outlet
Vacuum Blower Package

- Belt Drive With Guard
- Safety Filter / Silencer / Vacuum Breaker
- Blower
- Blower Outlet
- Outlet Silencer
1 - Case
2 - Heat Dissipation Ribs
3 – Bearing Housing
4 - Oil Fill
5 - End Plate
6 – Shaft Splines For Timing Gears
Rotary Valve Venting

Coperion K-TRON Aerolock

Vented Shear Protector
• Reduce Batch Cycle Time

• Reduce Energy Cost Per Batch

• Minimize VCM Exposure Risk To Personnel