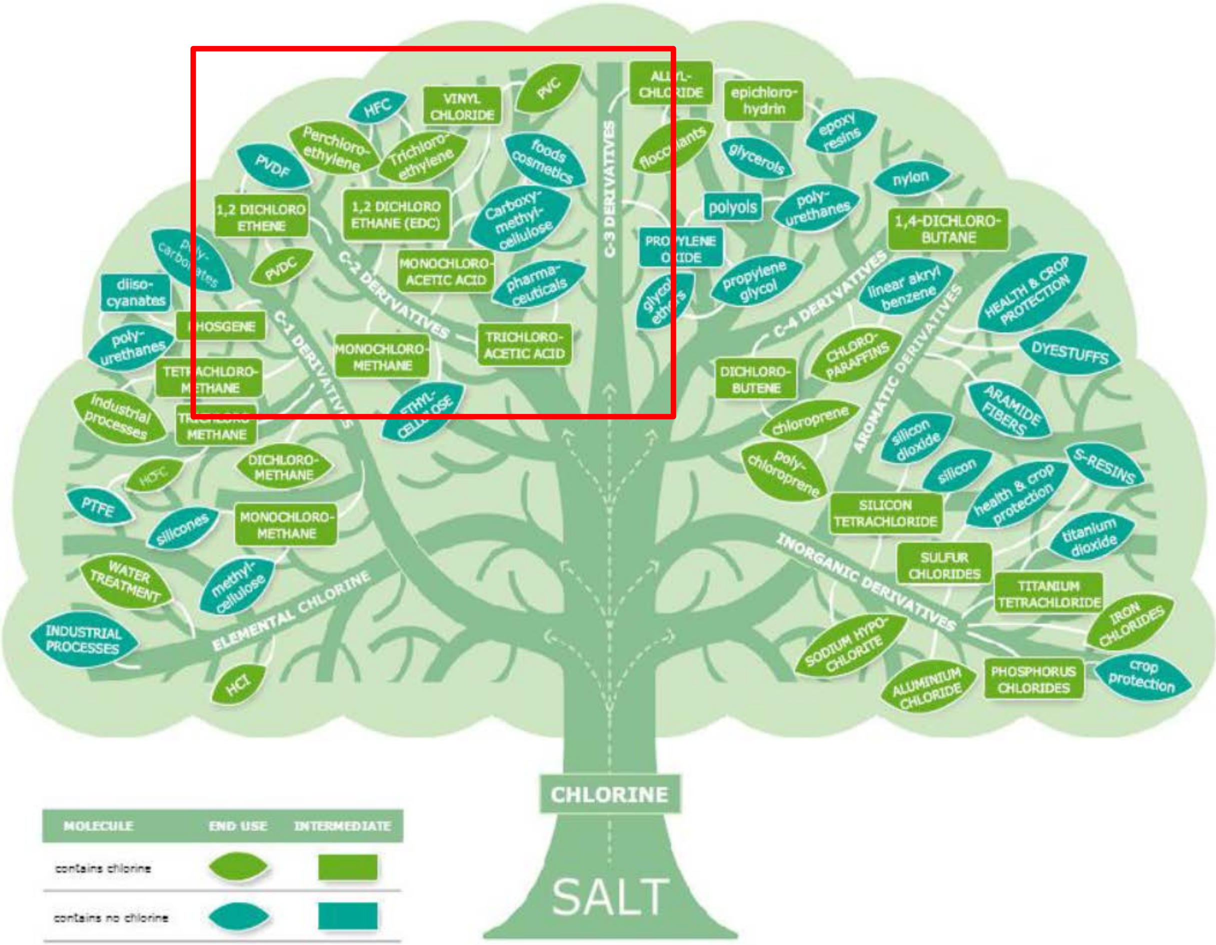
# Polyvinyl Chloride

# Objectives

- 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

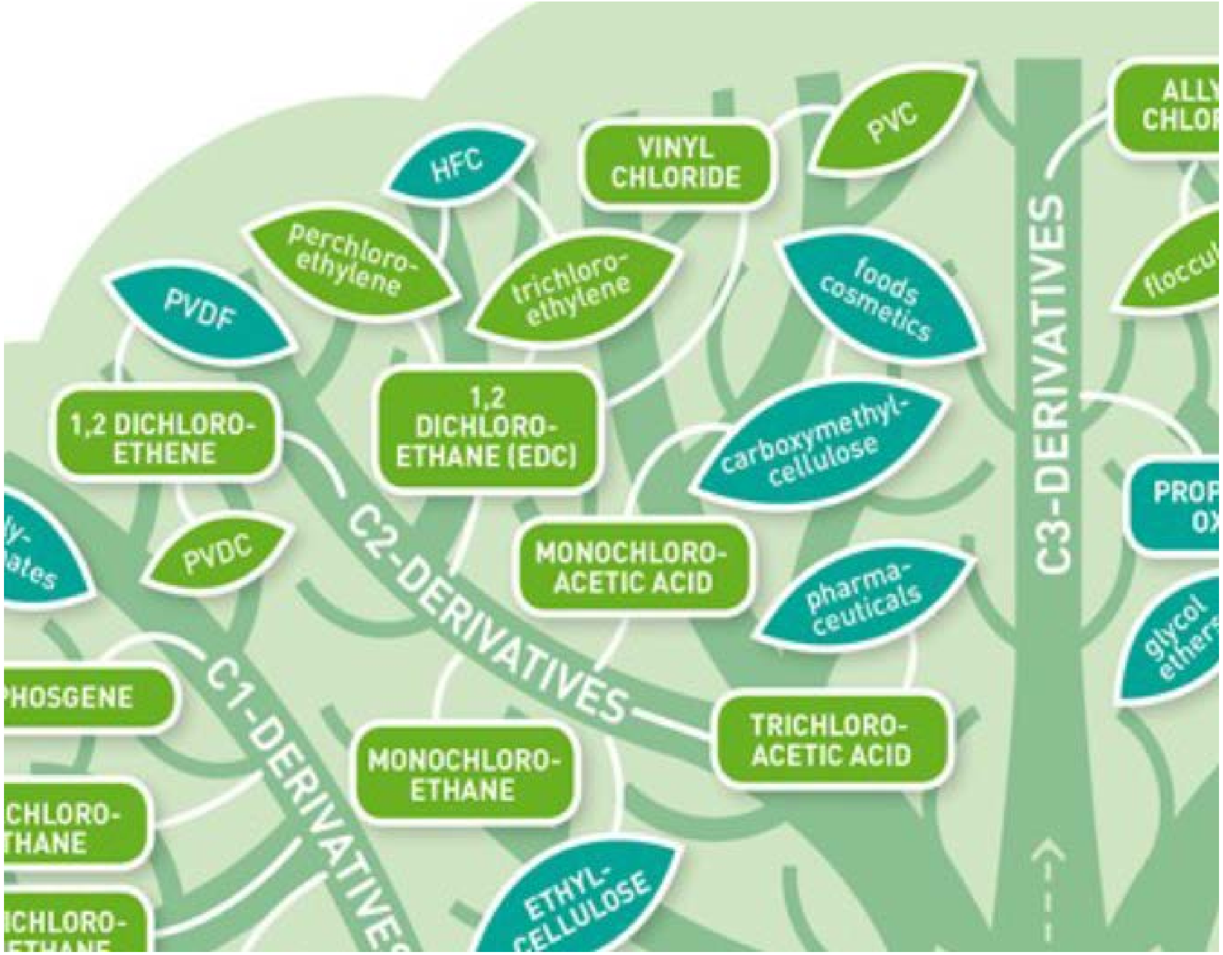
# Chlorine

# Chlorine Tree

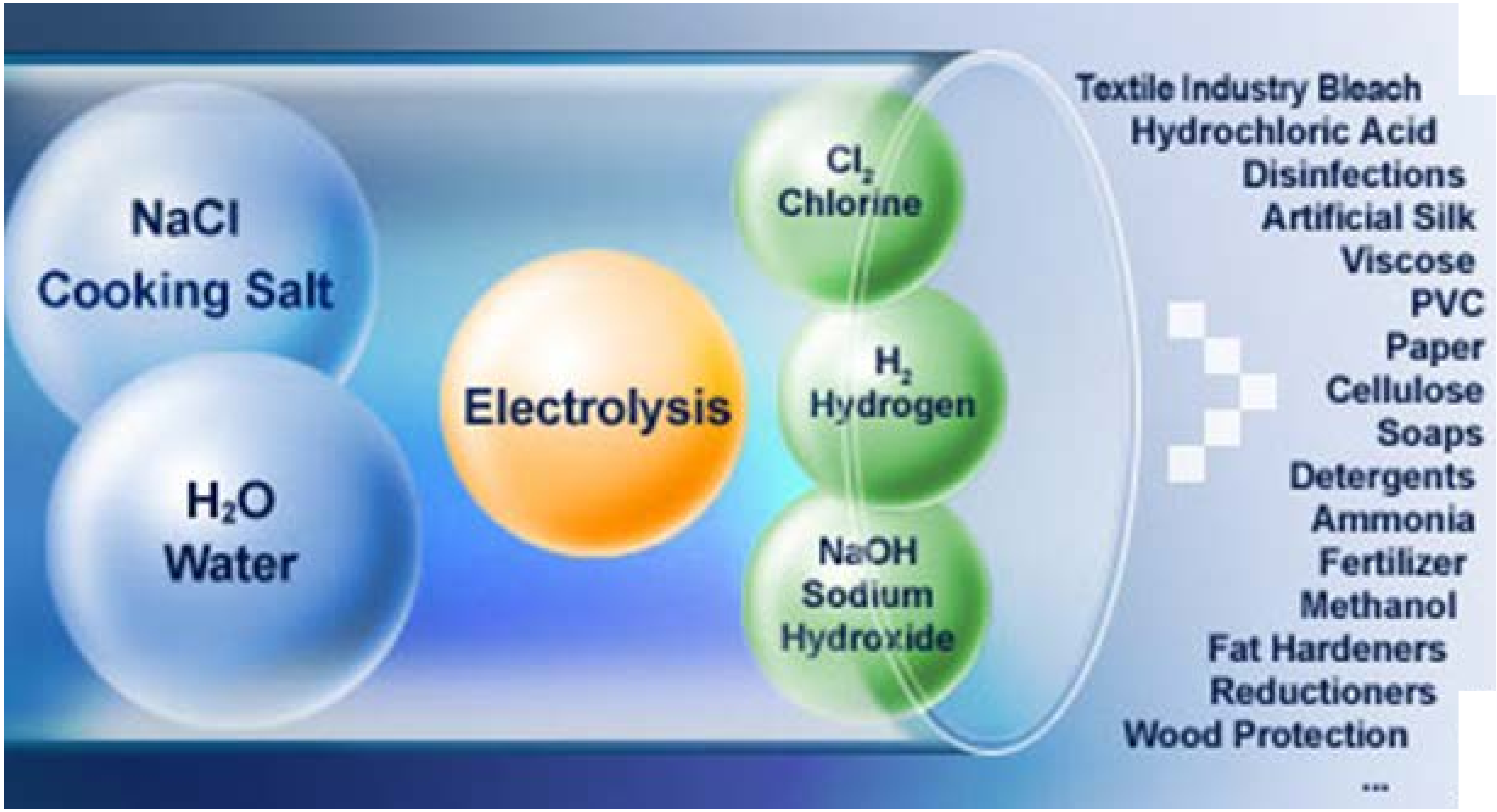



eurochlor.org

# Chlorine Tree – C2 Derivatives

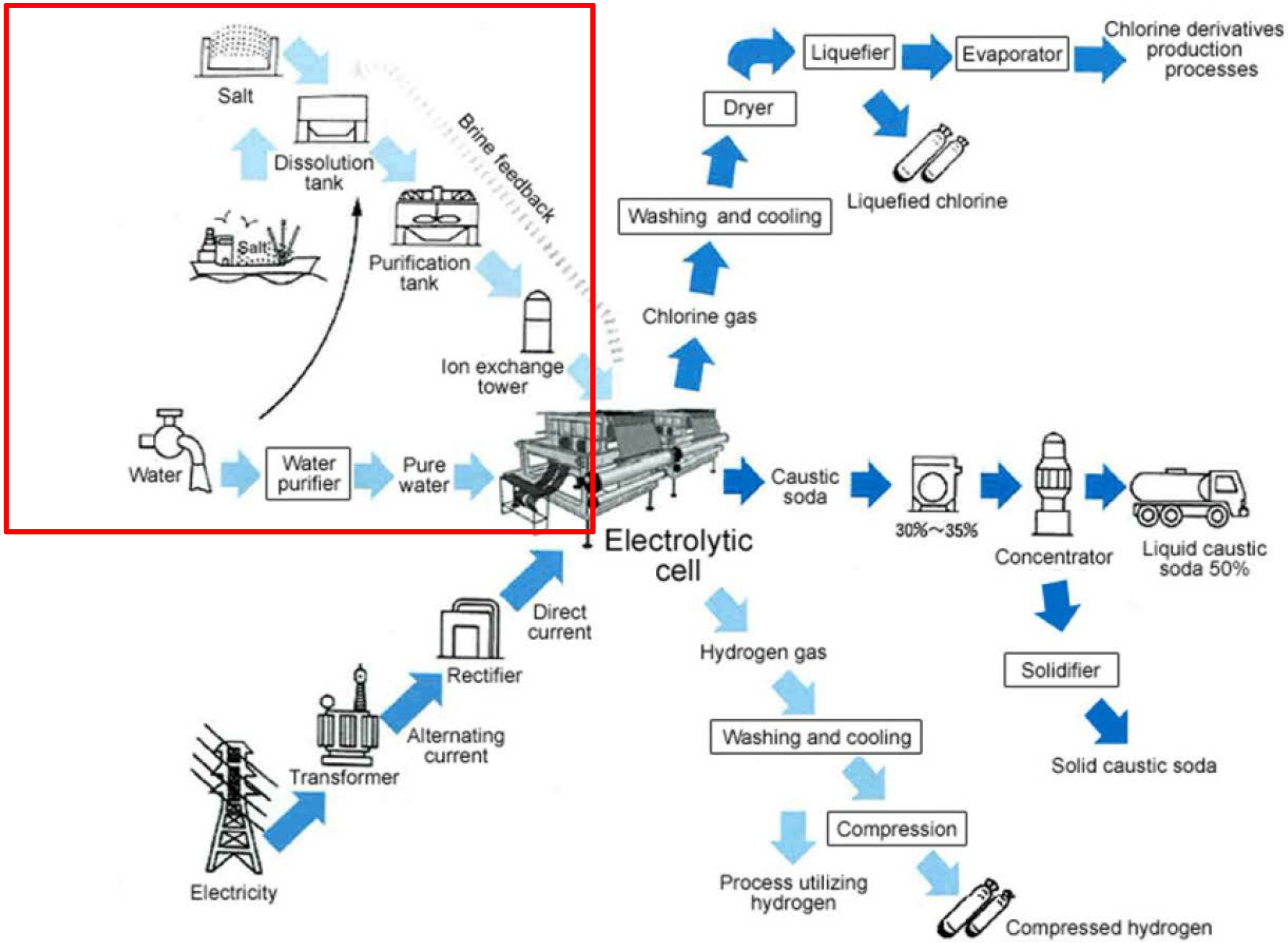


# Caustic-Chlorine



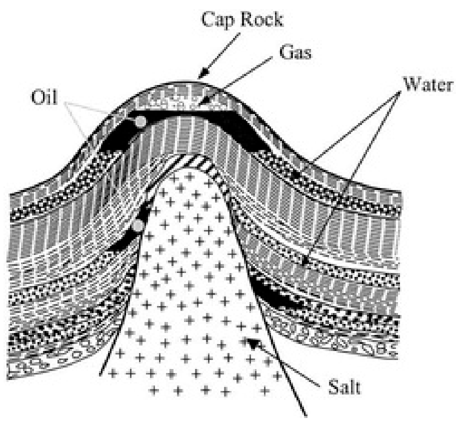

Siemens

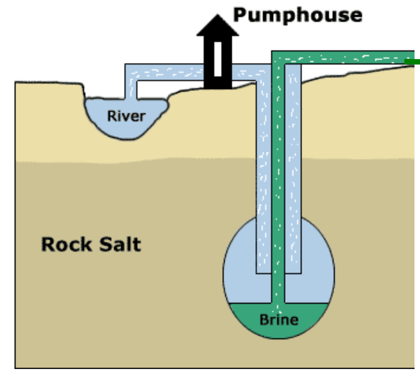
# Caustic - Chlorine Process

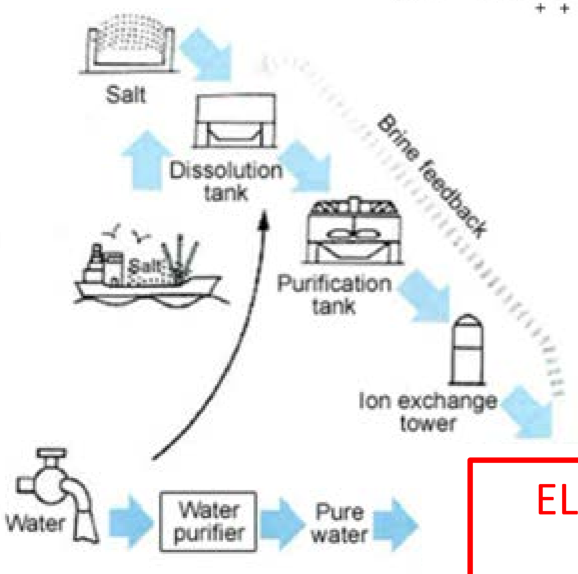



Markel Eclipse Membranes Brochure

# Salt Dome To Electrolytic Cell



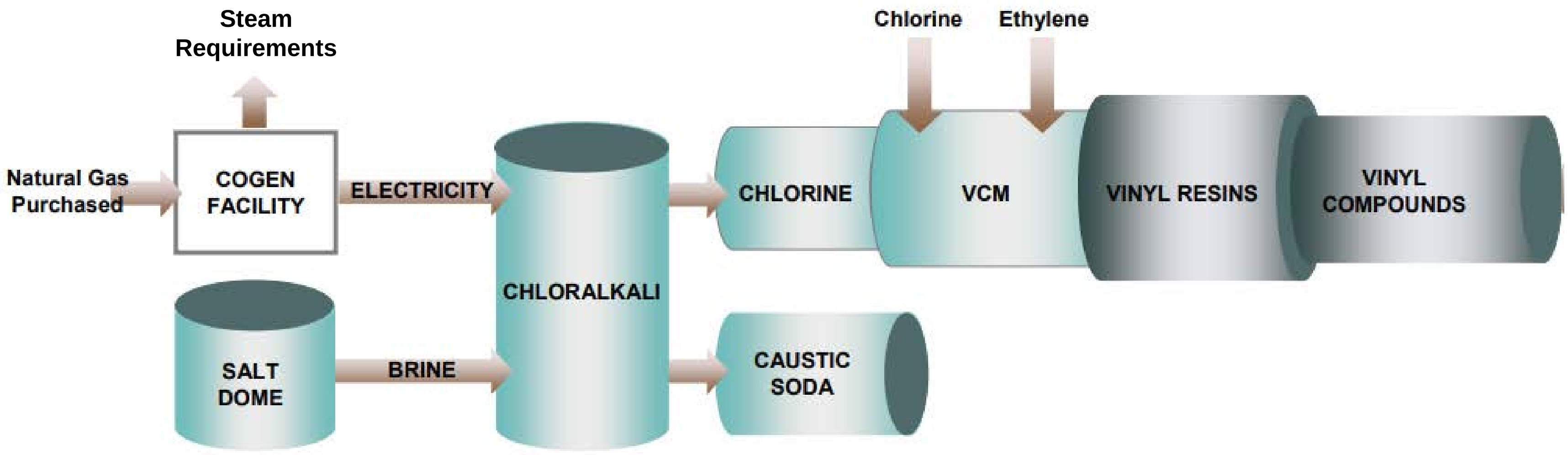




BRINE STORAGE

BRINE PURIFICATION

ELECTROLYTIC CELL

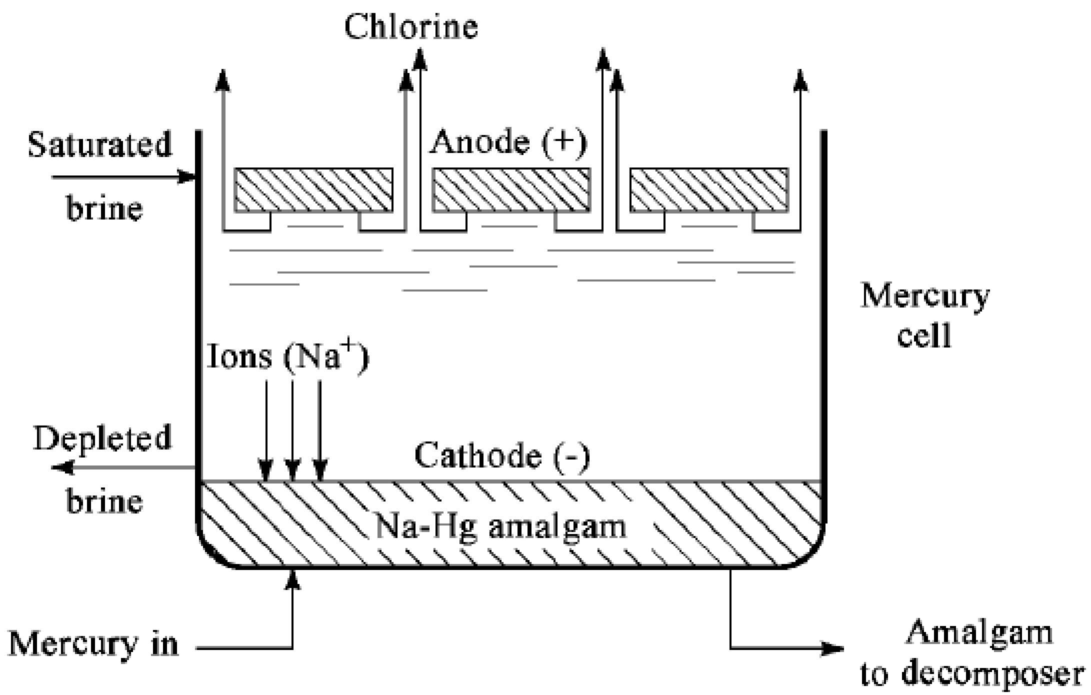
# Chlorovinyls



# Electrolytic Cell Technology

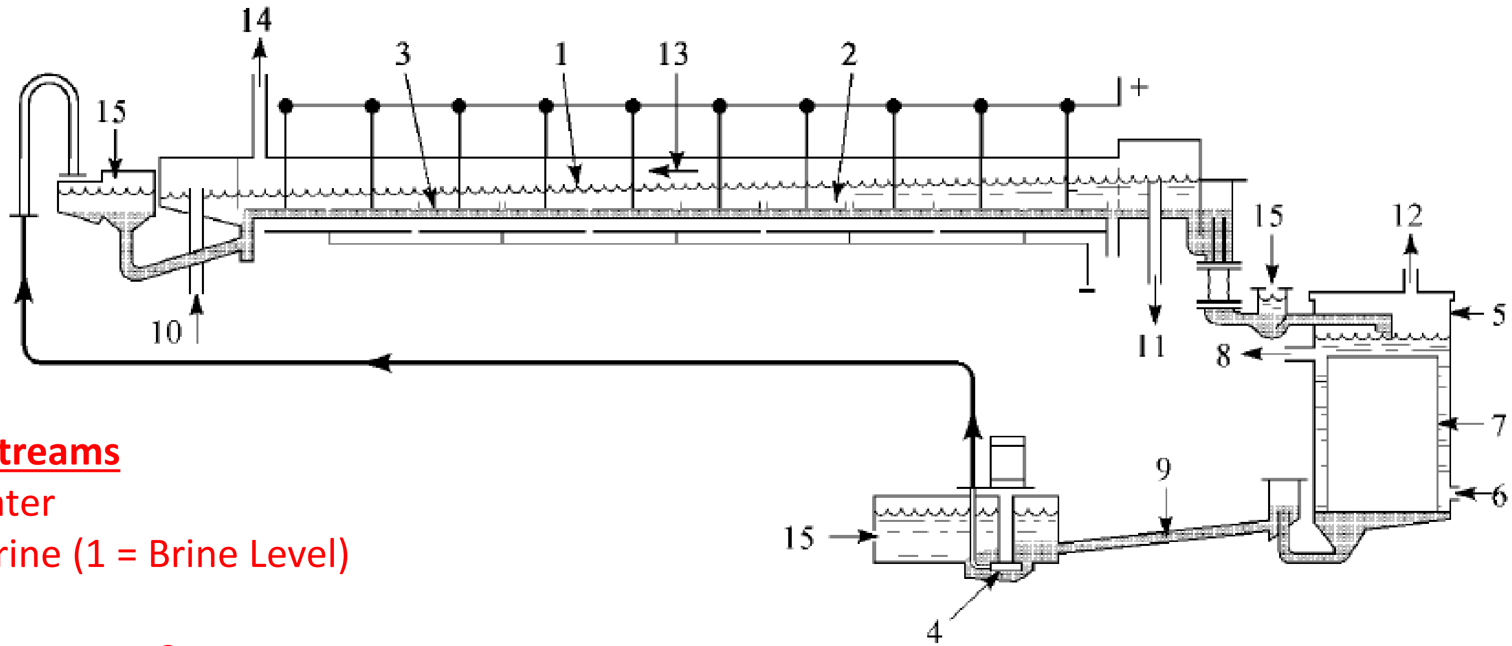
- Mercury
- Diaphragm
- Membrane

# Mercury Electrolytic Cell




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

# Mercury Recycle




**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

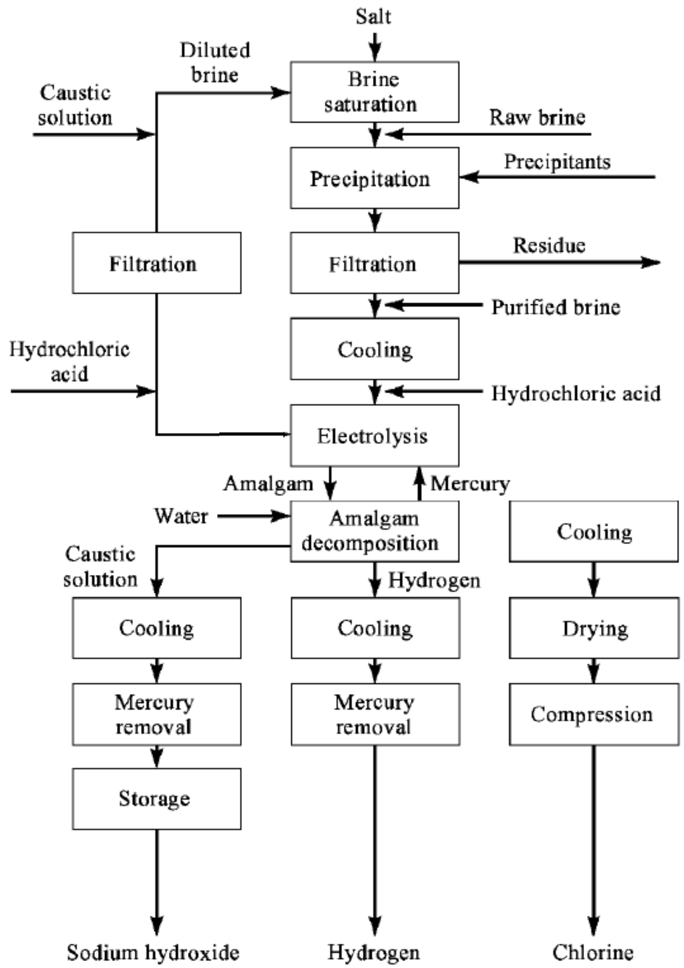
12 – Hydrogen

14 – Chlorine (13 = Chlorine Vapor)

15 – Wash Water

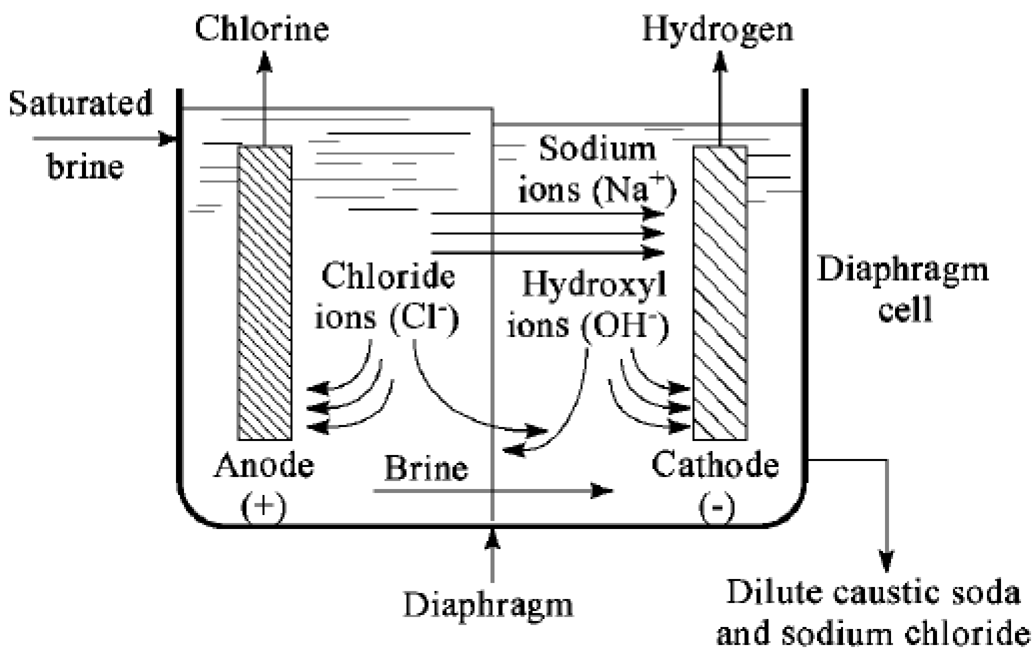
**Chlorine and Sodium Hydroxide**, Kirk-Othmer 4 Ed.

# Caustic-Chlorine Process – Mercury



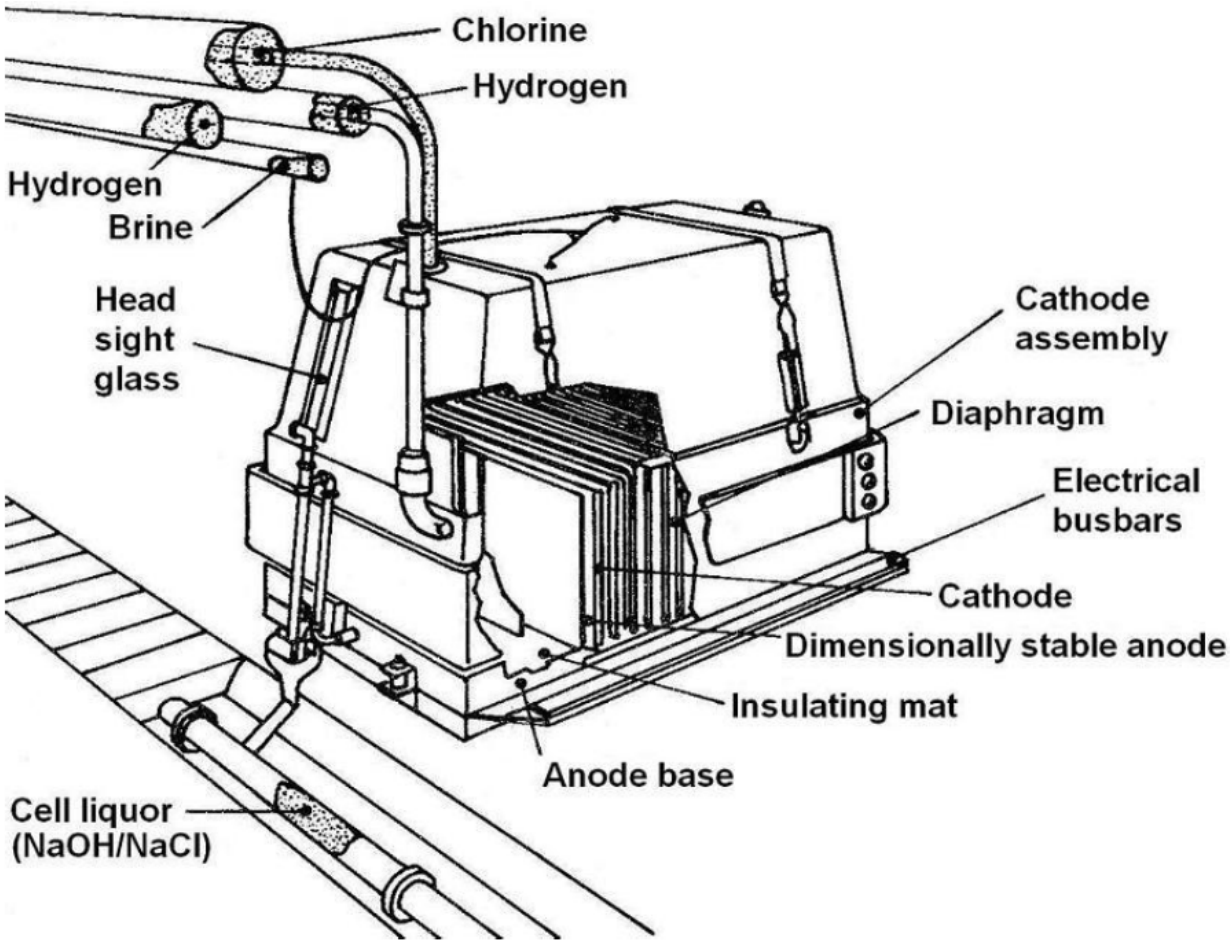

**Chlorine and Sodium Hydroxide**, Kirk-Othmer 4 Ed.

# Diaphragm Electrolytic Cell




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

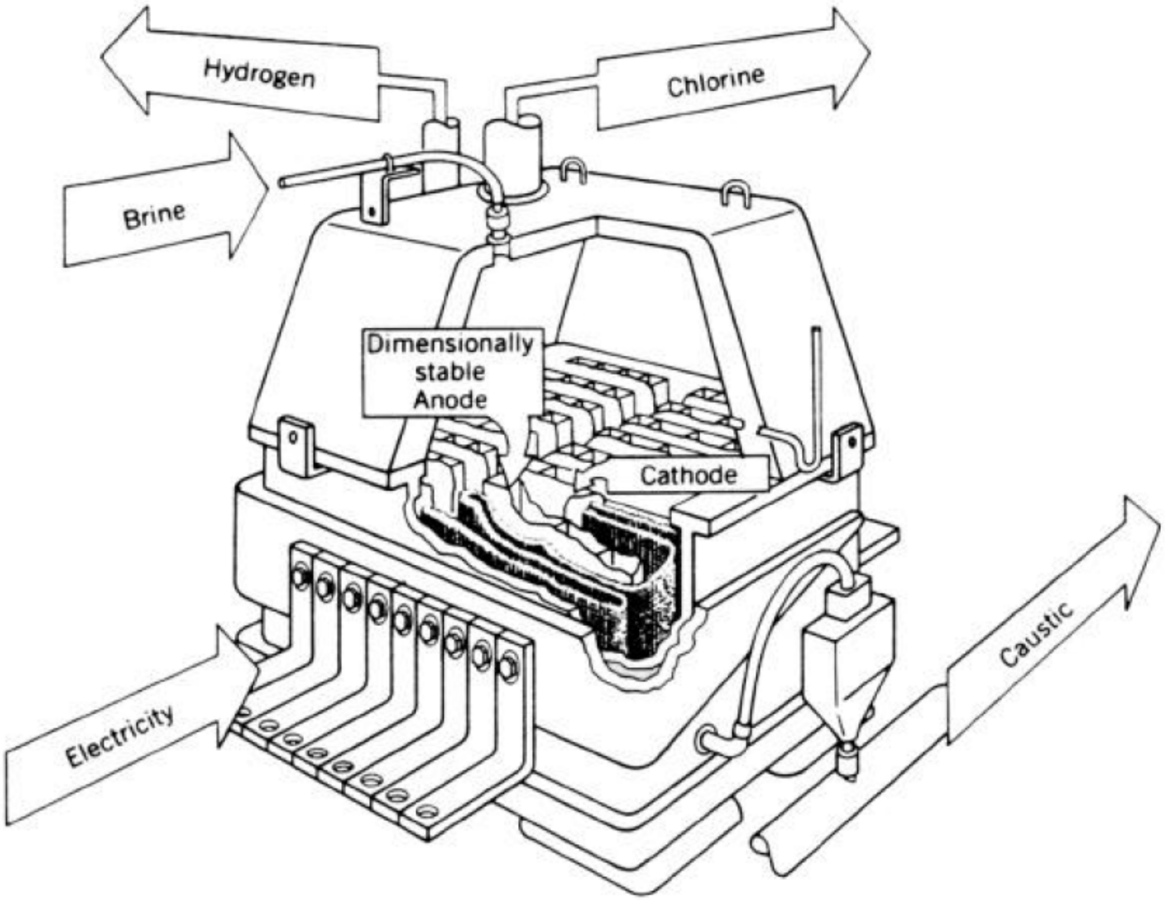
# Diaphragm Electrolytic Cell




<u>Production Chlor-Alkali – Best Available Techniques</u>, JRC 2014

# Diaphragm Electrolytic Cell

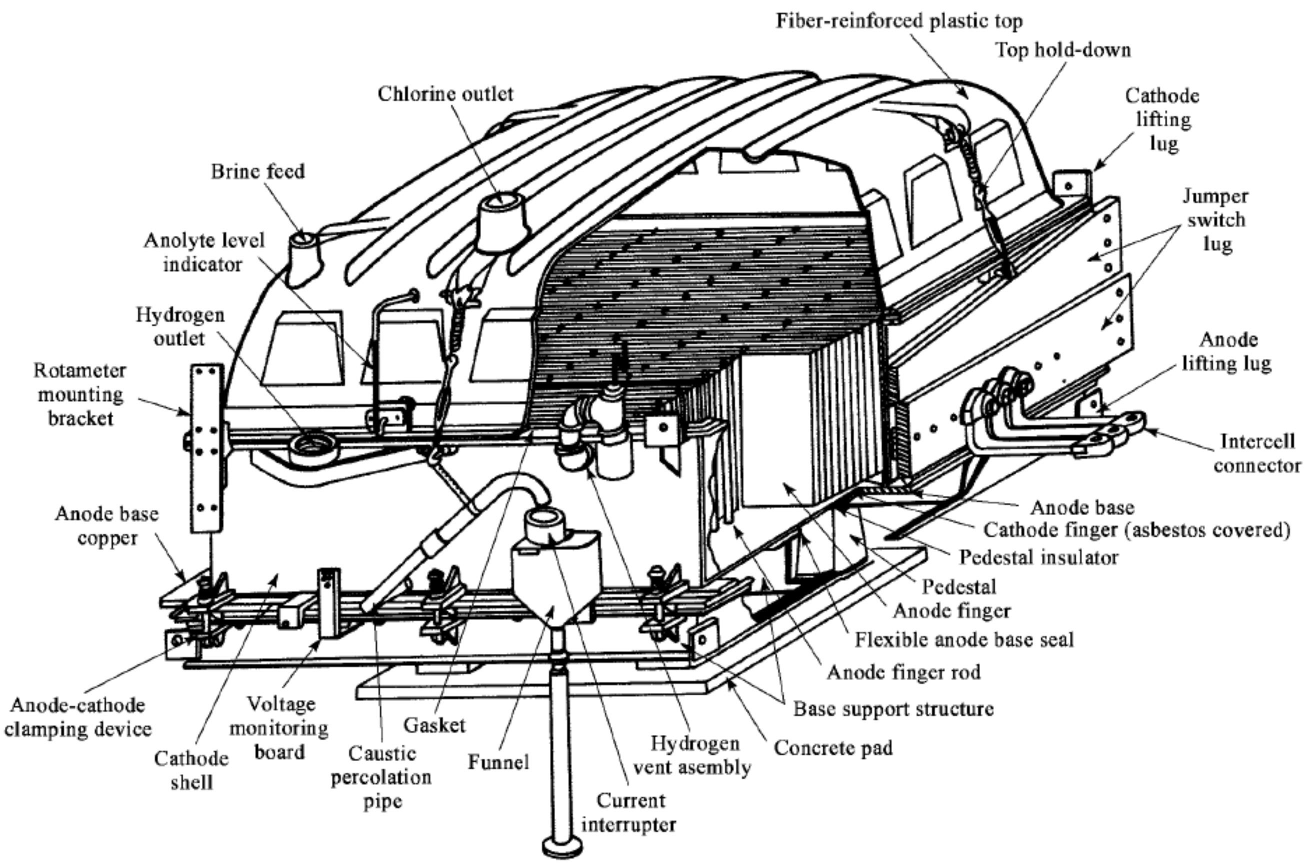
Diamond MDC Type




**Chlor-Alkali Industry - Energy and Environmental Profile Of US Chemical Industry,** Chapter 6

# Diaphragm Electrolytic Cell

Hooker H Type




Chlorine and Sodium Hydroxide, Kirk-Othmer 4 Ed.

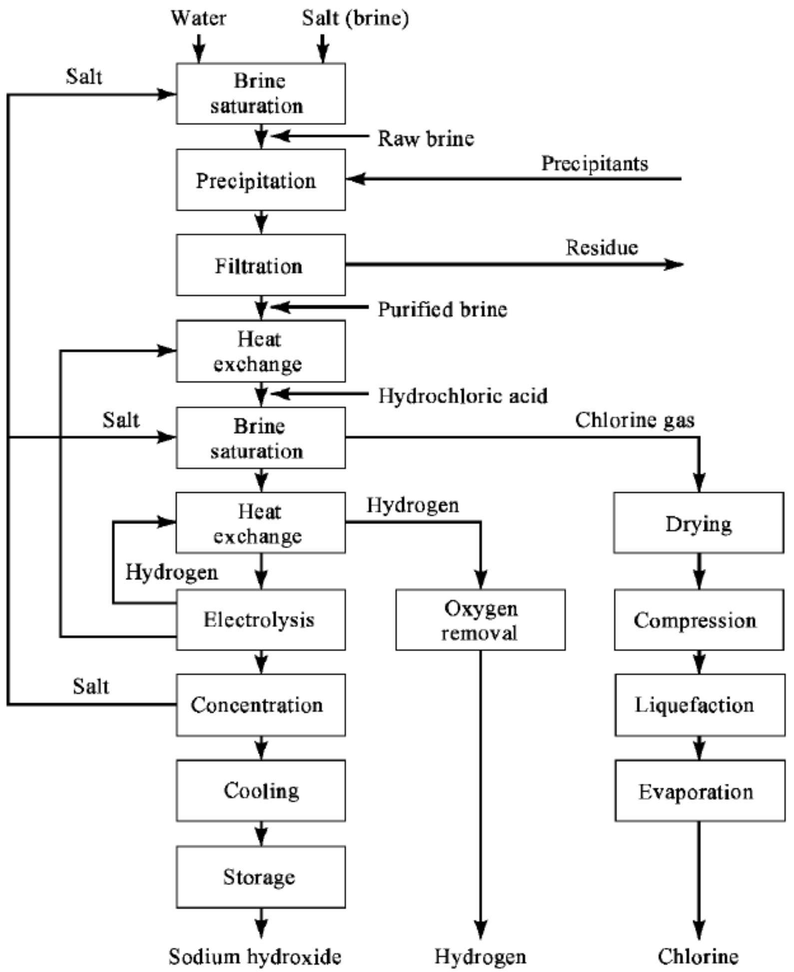
# Diaphragm Cell Row

**Occidental**

# Diaphragms

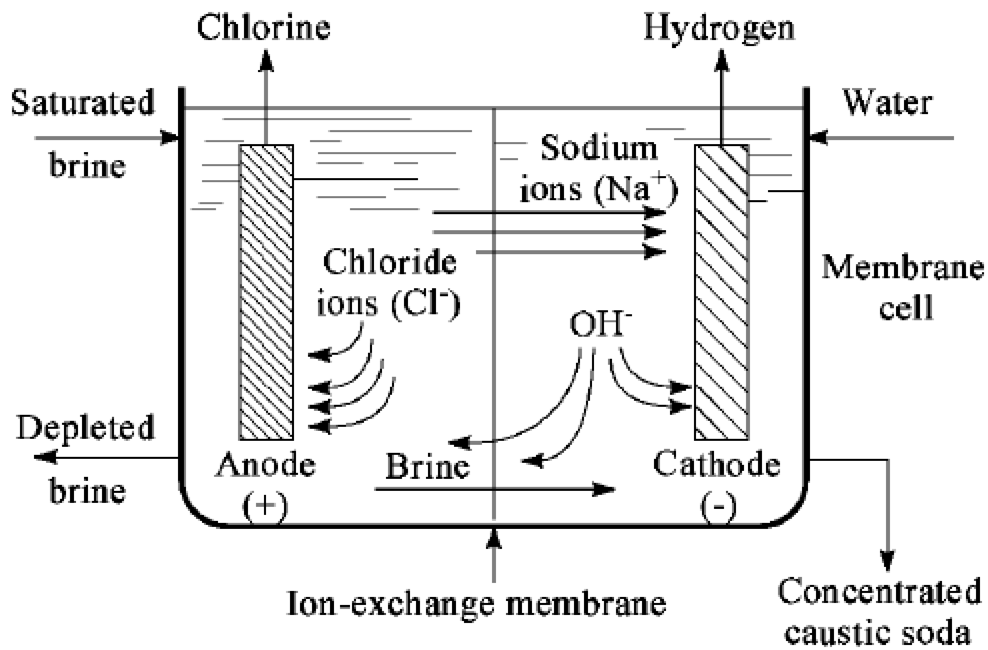
- **Diaphragm**
  - Originally Asbestos
  - Tephram (Non-Asbestos)
  - Polyaramix (Non-Asbestos)
  - Life:  200 to 400 Days
- **Anode Electrodes**
  - Coated Titanium
  - 8 to 15 Years
- **Cathode Electrodes**
  - Carbon Steel
  - 5 to 15 Years

# Caustic-Chlorine Process – Diaphragm



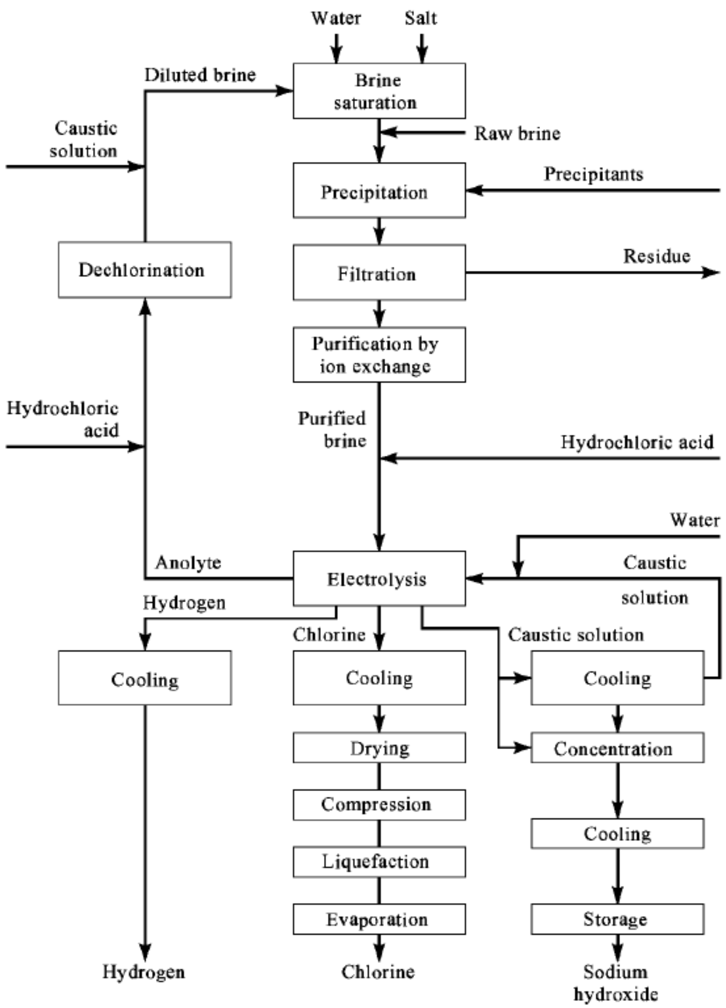

**Chlorine and Sodium Hydroxide**, Kirk-Othmer 4 Ed.

# Membrane Electrolytic Cell




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

# Caustic-Chlorine Process – Membrane




Chlorine and Sodium Hydroxide, Kirk-Othmer 4 Ed.

# Cell Technology Comparison

| Table 6-1. Characteristics of Various Chlorine/Sodium Hydroxide Electrolysis Cells | | | |
|---|---|---|---|
| **Component** | **Diaphragm Cell** | **Mercury Cell** | **Membrane Cell** |
| Cathode | Steel/steel coating with nickel | Mercury flowing over steel | Steel or nickel with a nickel-based coating |
| Anode | Titanium with ruthenium and titanium oxide coatings; iridium oxide added to improve performance and extend life | Titanium with ruthenium and titanium oxide coatings; iridium oxide added to improve performance and extend life | Titanium with ruthenium and titanium oxide coatings; iridium oxide added to improve performance and extend life |
| Diaphragm/ Membrane Material | Asbestos and fibrous polytetrafluoroethylene | None | Ion-exchange membrane (fluorinated polymers) |
| Cathode Product | 10 to 15% sodium hydroxide solution, containing 15 to 17% salt (NaCl) (sent to evaporator for further processing); hydrogen gas | Sodium amalgam (sent for further processing through a decomposer cell) | 30-33% sodium hydroxide solution (sent to evaporator for further processing); hydrogen gas |
| Anode Product | Chlorine gas containing some oxygen, salt, water vapor, and sodium hydroxide | Chlorine gas containing some oxygen, salt, and water vapor | Chlorine gas containing some oxygen, salt, and water vapor |
| Evaporator/Decom-position Product | 50% sodium hydroxide solution containing 1% salt; solid salt from evaporator | 50% sodium hydroxide solution; hydrogen gas | 50% sodium hydroxide solution with very little salt |
| Electricity Consumption | 2,550 to 2,900 kWh/ton chlorine gas | 3,250 to 3,450 kWh/ton chlorine gas | 2,530 to 2,600 kWh/ton chlorine gas |

Sources: Sittig 1977, EPA 1990, EPA 1992b, EPA 1995b, DOW 1999.

**The Chlor-Alkali Industry**, Ch. 6 - Energy and Environmental Profile Of US Chemical Industry

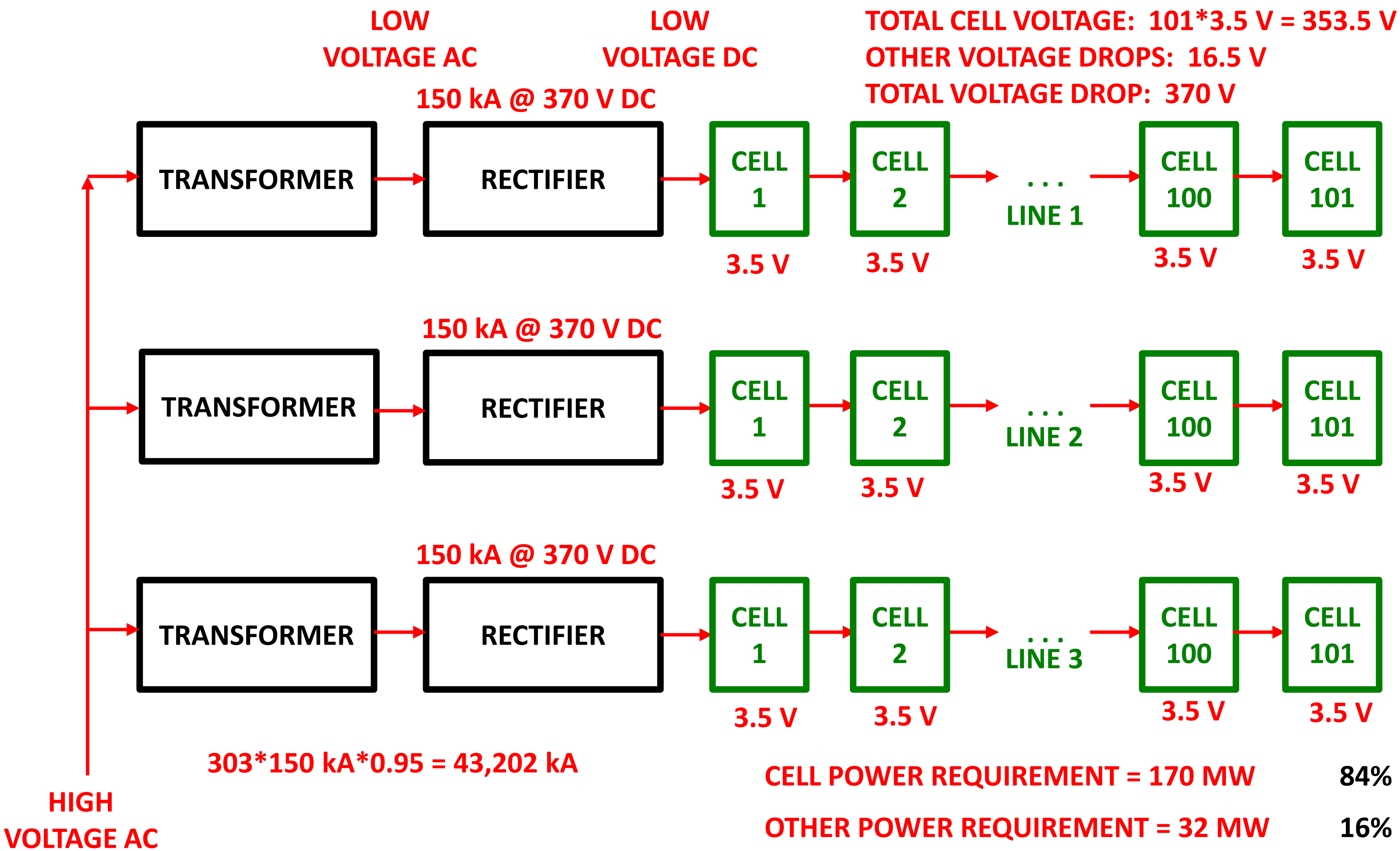
# Cell Technology Comparison

| | Mercury cell | Diaphragm cell | Membrane cell |
|---|---|---|---|
| Cell voltage/V | −4.4 | −3.45 | −2.95 |
| Current density/A $cm^{-2}$ | 1.0 | 0.2 | 0.4 |
| Current efficiency for $Cl_2$/% | 97 | 96 | 98.5 |
| Energy consumption/kWh per ton of NaOH | | | |
| (a) Electrolysis only | 3150 | 2550 | 2400 |
| (b) Electrolysis + evaporation to 50% NaOH | 3150 | 3260 | 2520 |
| Purity $Cl_2$/% | 99.2 | 98 | 99.3 |
| Purity $H_2$/% | 99.9 | 99.9 | 99.9 |
| $O_2$ in $Cl_2$/% | 0.1 | 1–2 | 0.3 |
| $Cl^-$ in 50% NaOH/% | 0.003 | 1–1.2 | 0.005 |
| Sodium hydroxide concentration prior to evaporation/% | 50 | 12 | 35 |
| Mercury pollution considerations | Yes | No | No |
| Requirement for brine purification | Some | More stringent | Very extensive |
| Production rate per single cell/tons NaOH per year | 5000 | 1000 | 100 |
| Land area for plant, of $10^5$ tons NaOH per year/$m^2$ | 3000 | 5300 | 2700 |

Teknik Elektrokimia

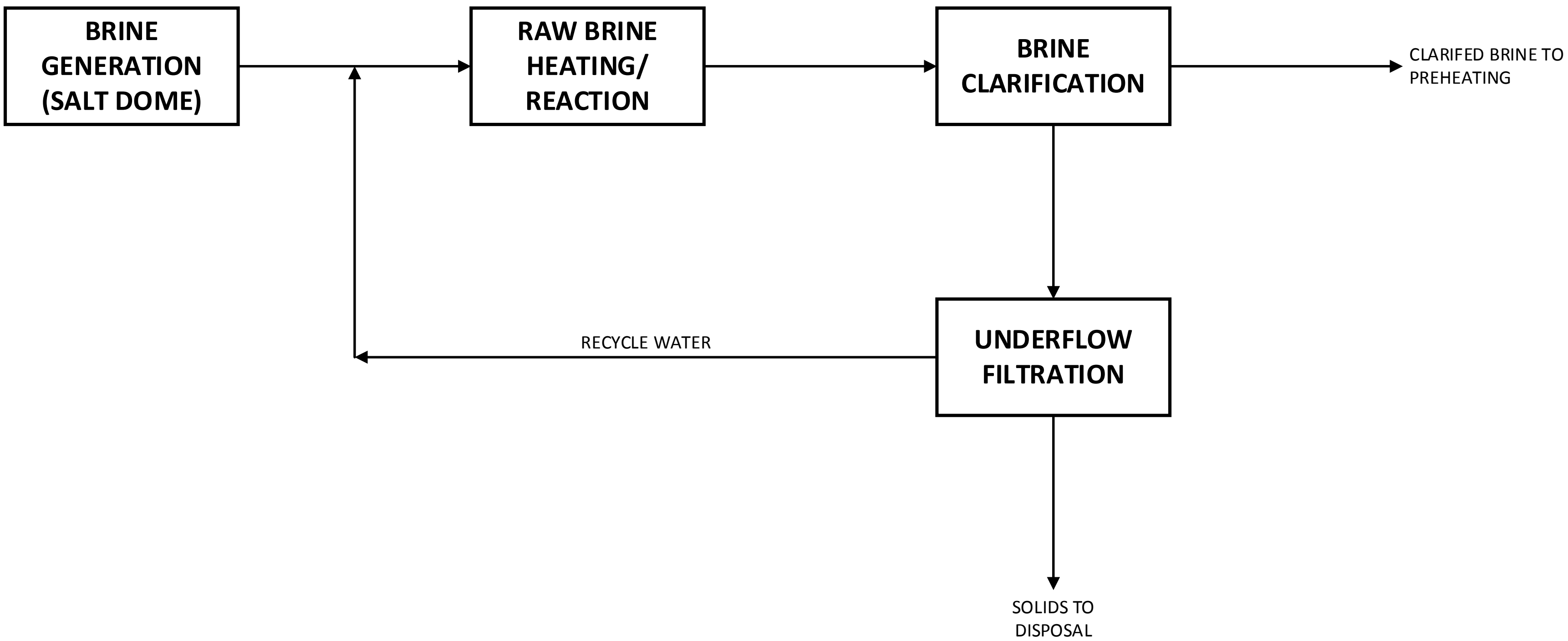
# Cell Power Distribution (1500 TPD $Cl_2$)

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

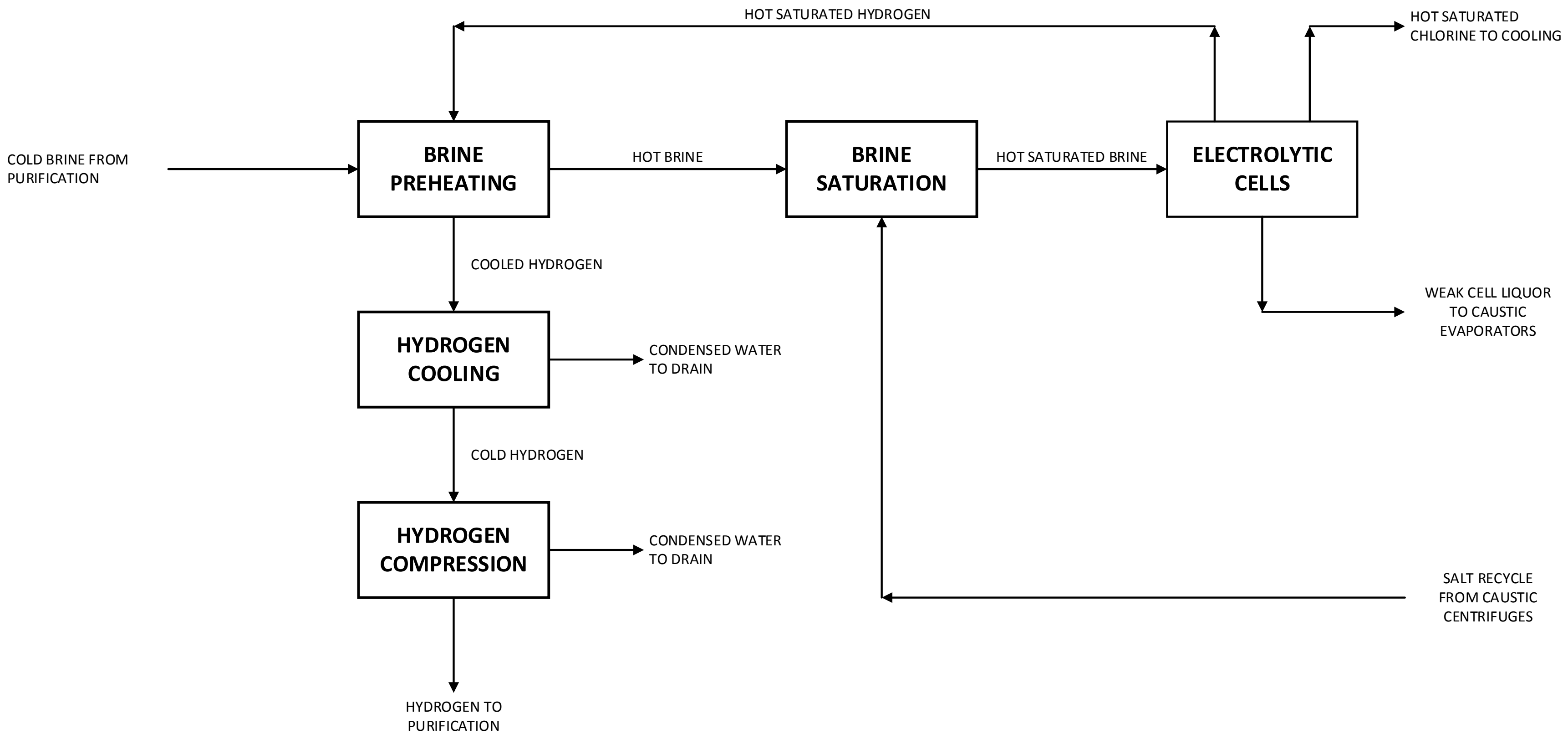



| | |
|---|---|
| CELL POWER REQUIREMENT = 170 MW | 84% |
| OTHER POWER REQUIREMENT = 32 MW | 16% |
| TOTAL POWER REQUIREMENT = 202 MW | 100% |

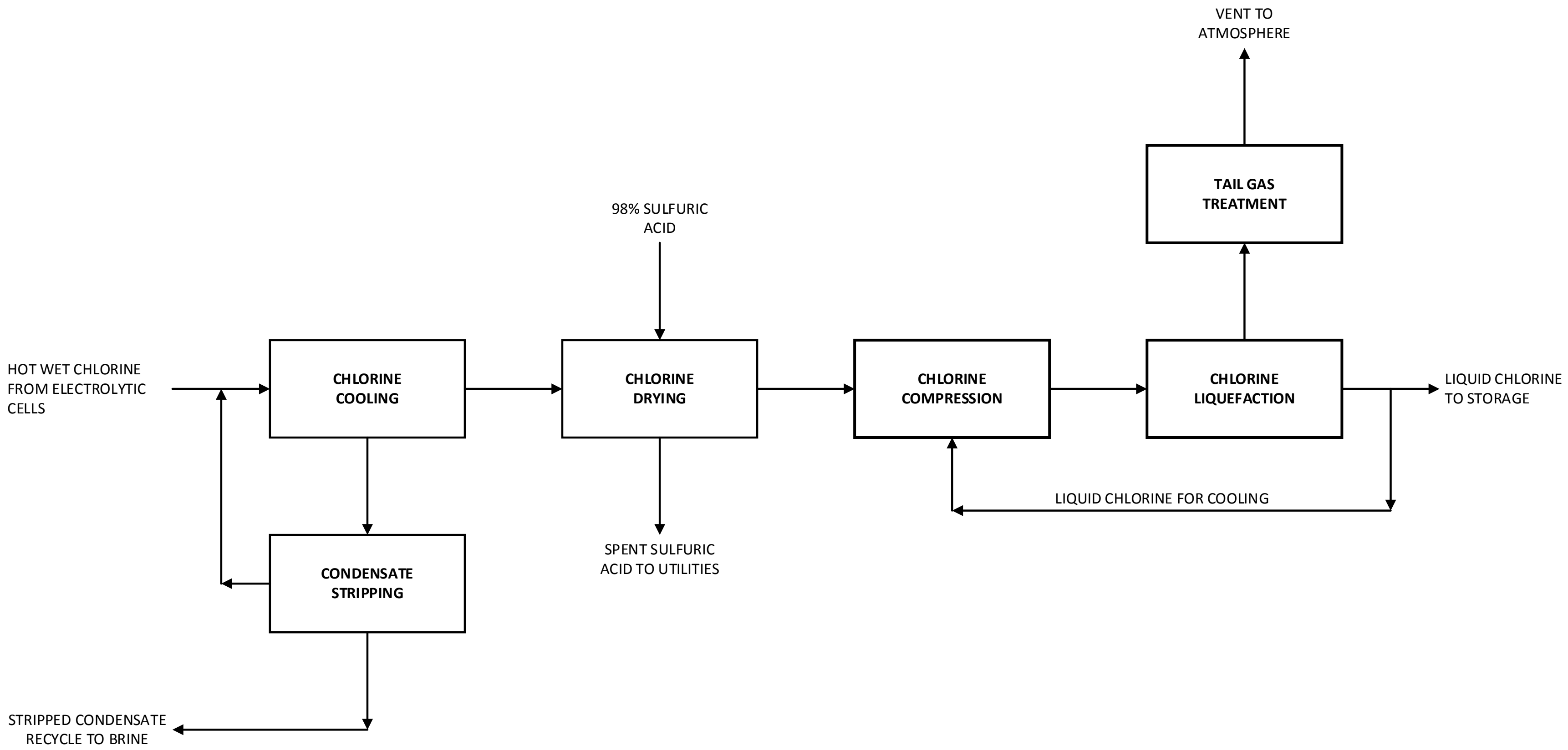
# Brine Treatment



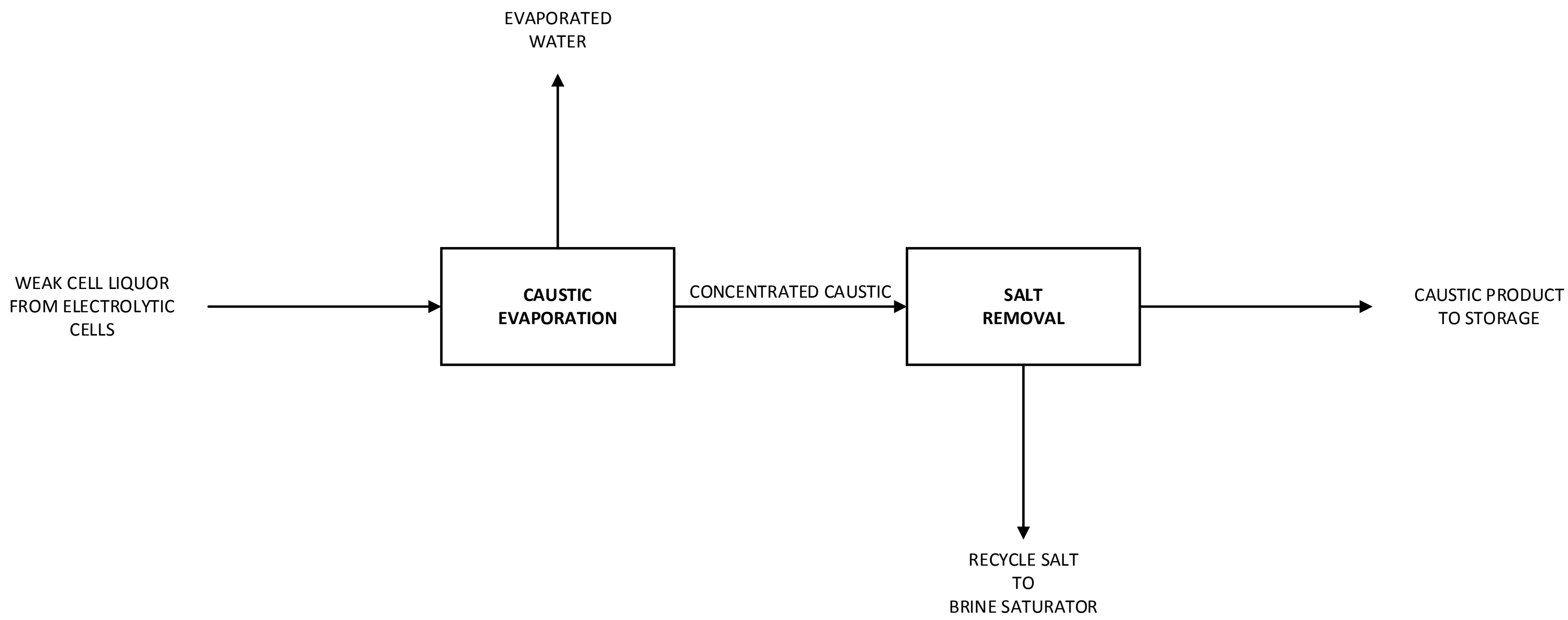
# Brine Conversion



# Chlorine


VENT TO ATMOSPHERE
TAIL GAS TREATMENT
98% SULFURIC ACID
HOT WET CHLORINE FROM ELECTROLYTIC CELLS
CHLORINE COOLING
CHLORINE DRYING
CHLORINE COMPRESSION
CHLORINE LIQUEFACTION
LIQUID CHLORINE TO STORAGE
LIQUID CHLORINE FOR COOLING
CONDENSATE STRIPPING
SPENT SULFURIC ACID TO UTILITIES
STRIPPED CONDENSATE RECYCLE TO BRINE

# Caustic


EVAPORATED WATER
WEAK CELL LIQUOR FROM ELECTROLYTIC CELLS
CAUSTIC EVAPORATION
CONCENTRATED CAUSTIC
SALT REMOVAL
CAUSTIC PRODUCT TO STORAGE
RECYCLE SALT TO BRINE SATURATOR

# Vinyl Chloride Monomer (VCM)

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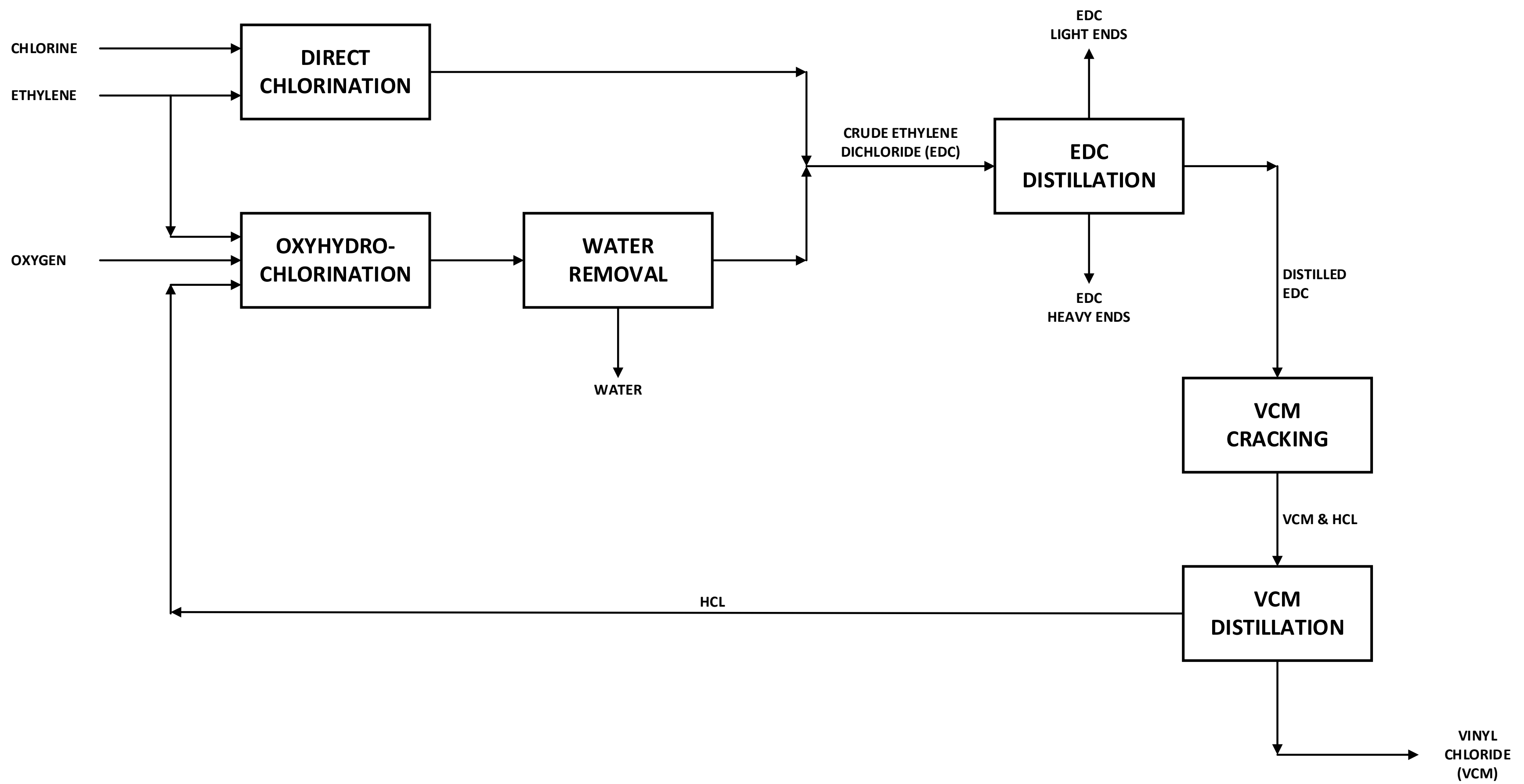
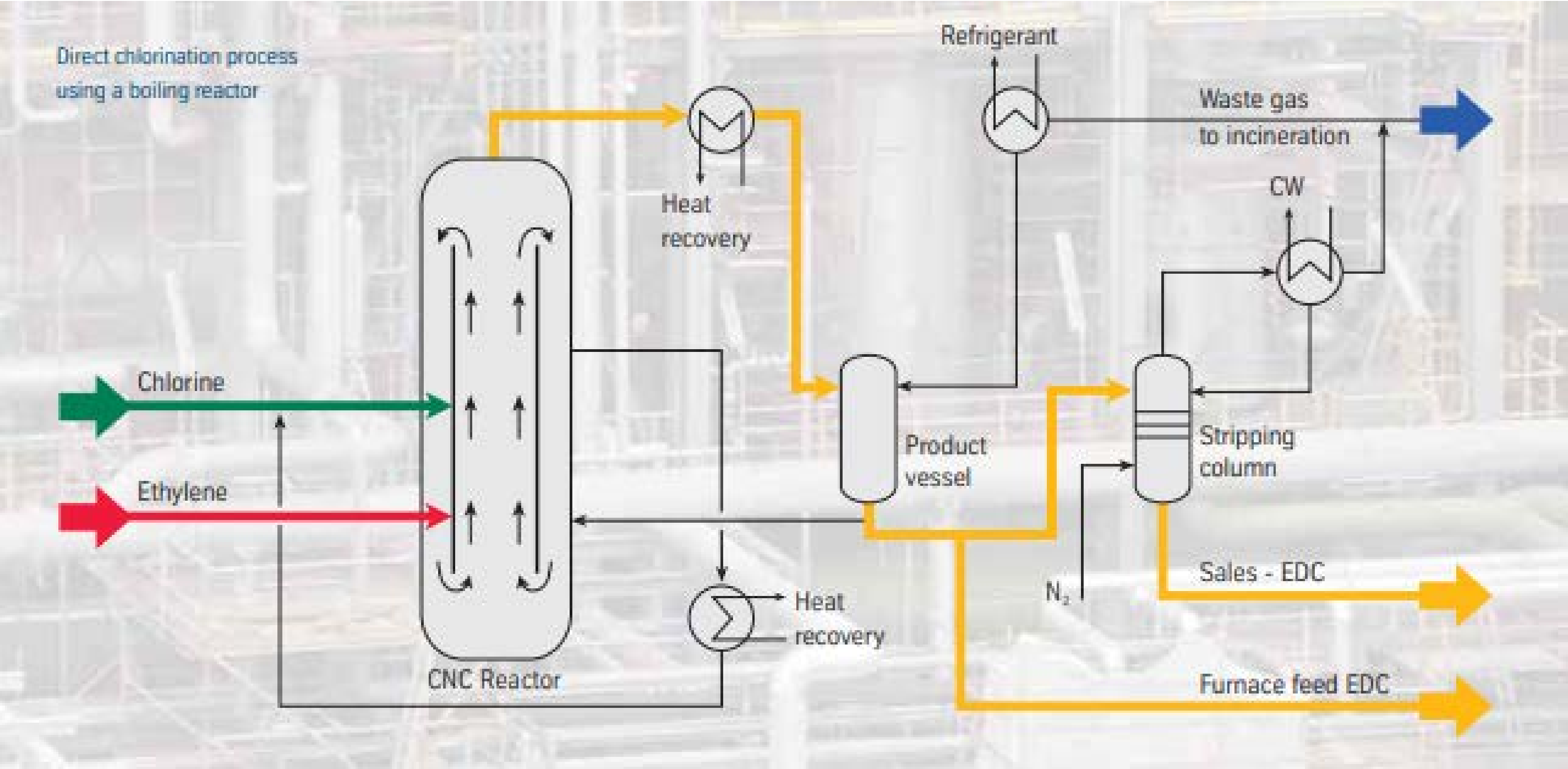
# VCM Overview

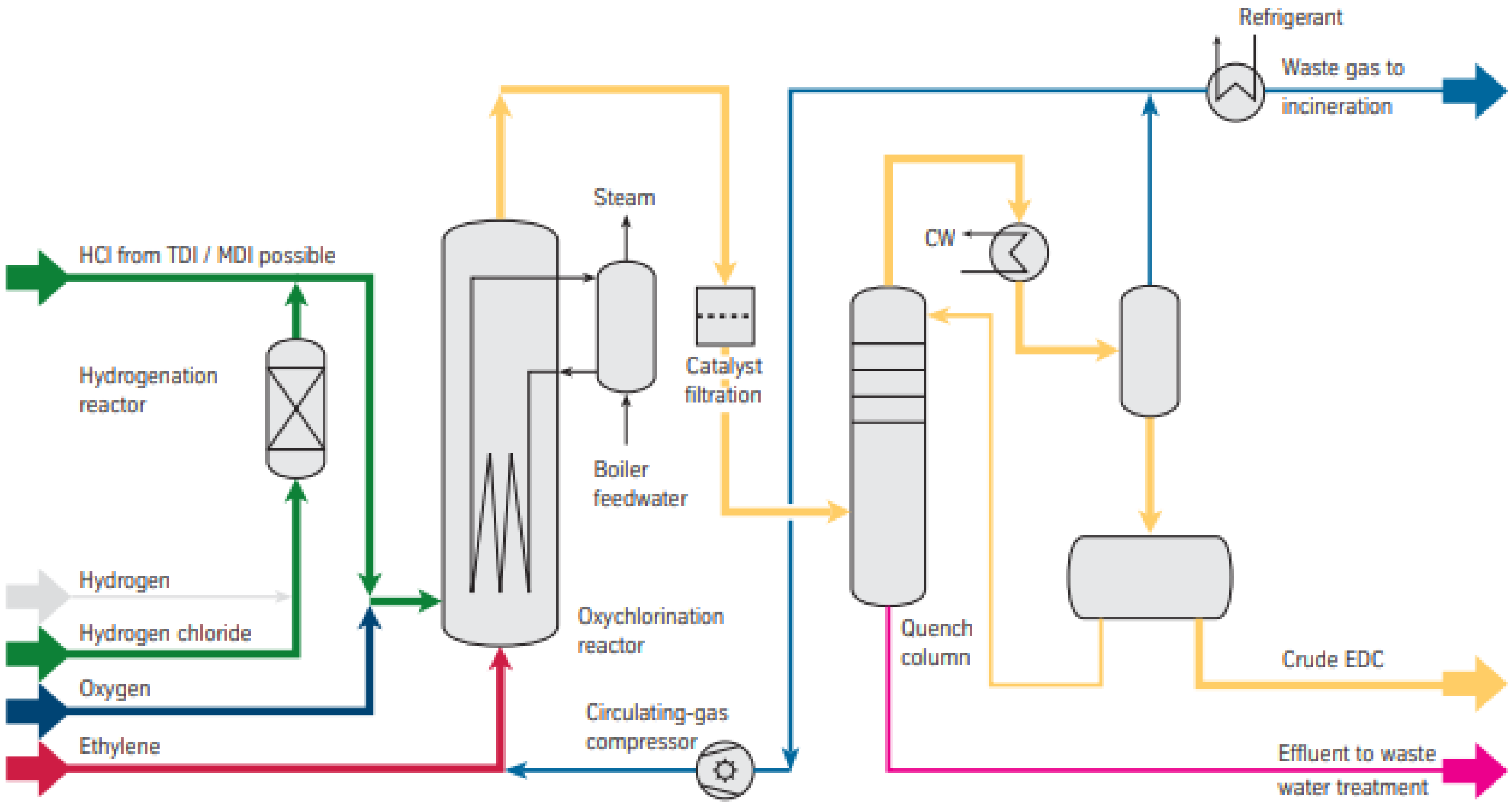


# Direct Chlorination



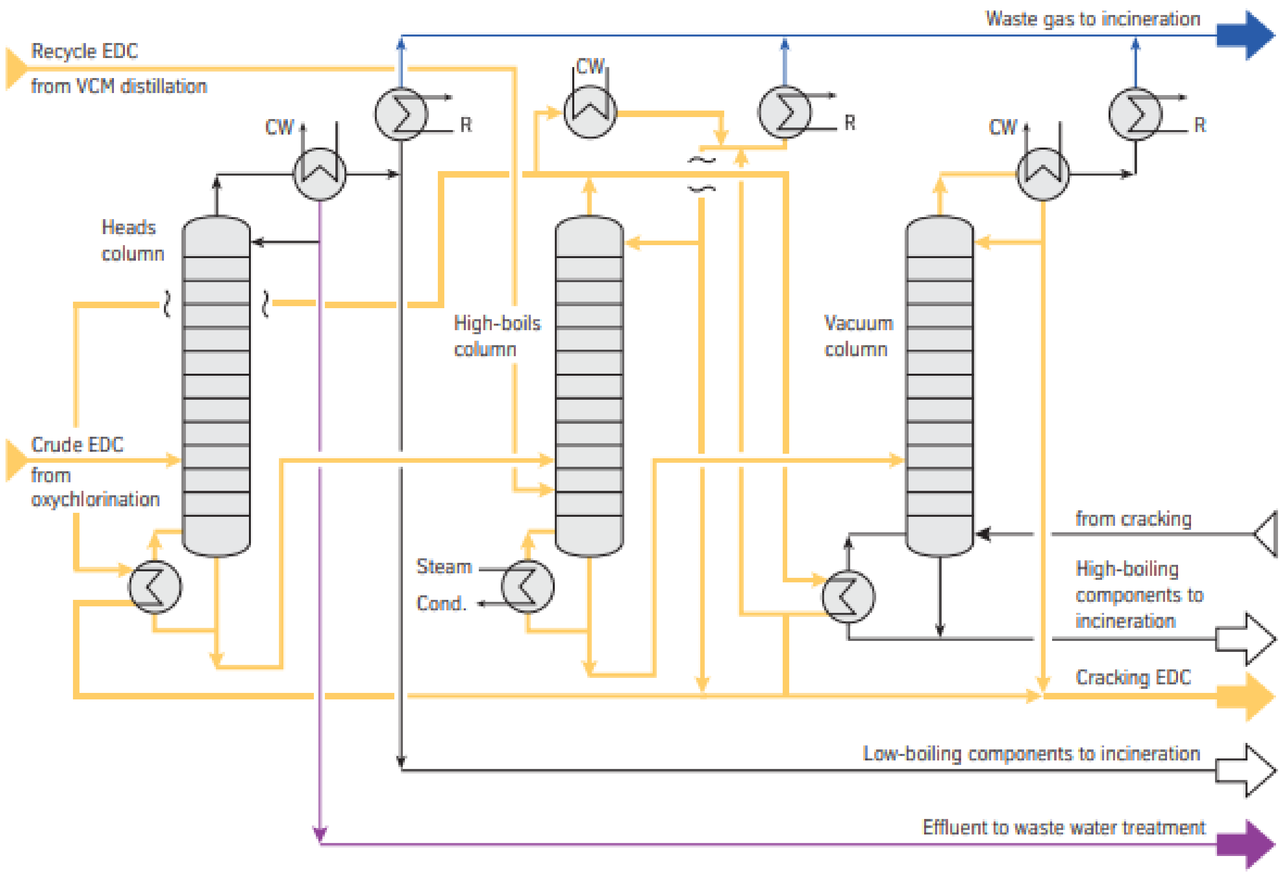

**Vinnolit VCM Process**

# Oxychlorination



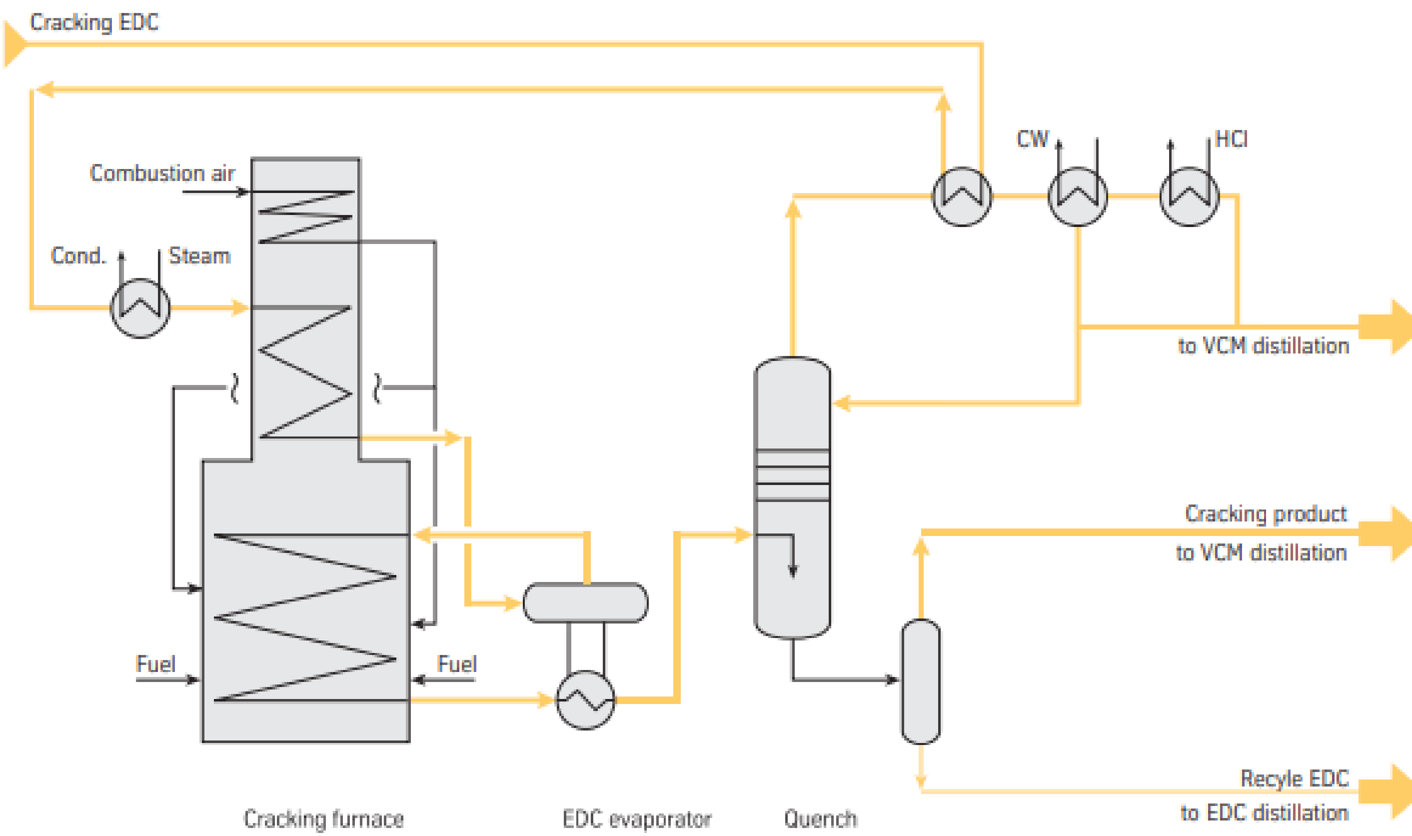

**Vinnolit VCM Process**

# EDC Distillation



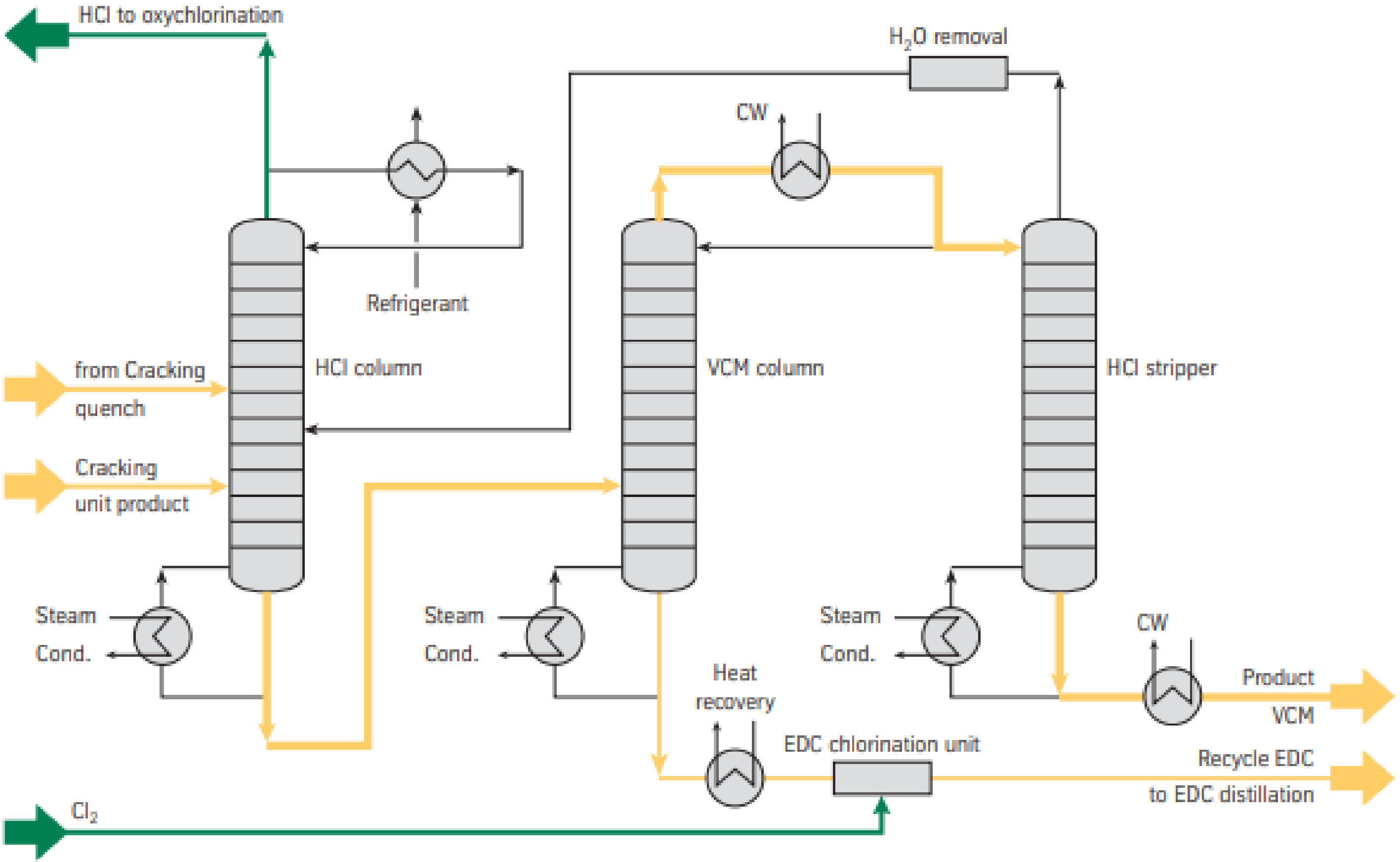

**Vinnolit VCM Process**

# VCM Cracking




**Vinnolit VCM Process**

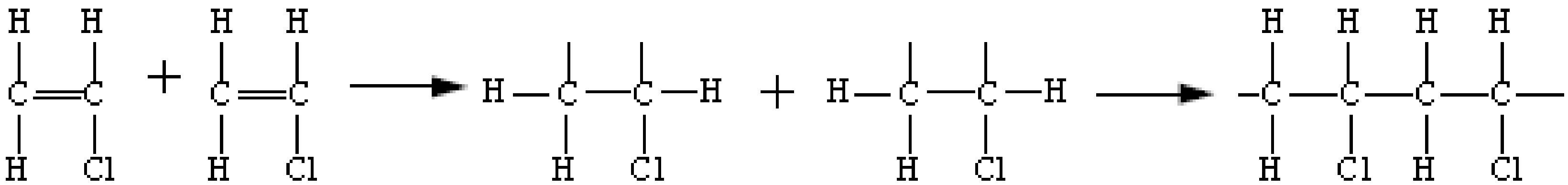
# VCM Distillation




**Vinnolit VCM Process**

# Polyvinyl Chloride (PVC)

# VCM Polymerization

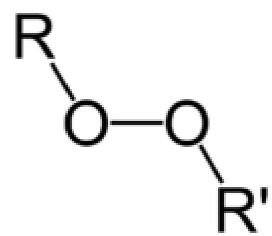


Vinyl Chloride

(VCM)

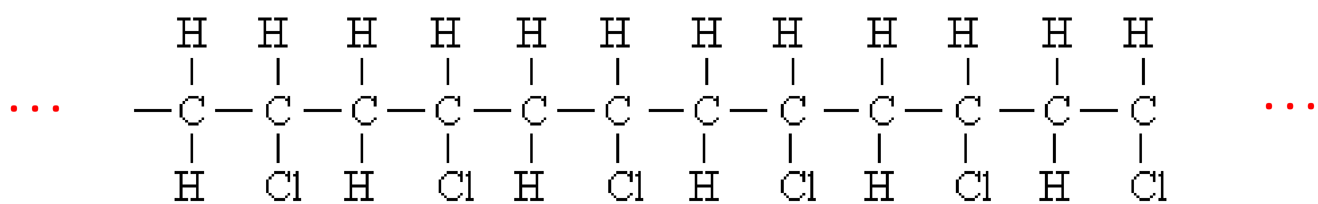
Poly Vinyl Chloride

(PVC)



Organic Peroxide

Initiator



# Plastic Types

- **Thermosetting**
  - Cross-Linking During Curing
  - High Temperature Applications
  - Polyurethane, Polyester, Vinyl Ester, Epoxy
- **Thermoplastic**
  - No Cross-Linking During Curing
  - Recyclable / Remoldable
  - Polyethylene, Polypropylene, **PVC**

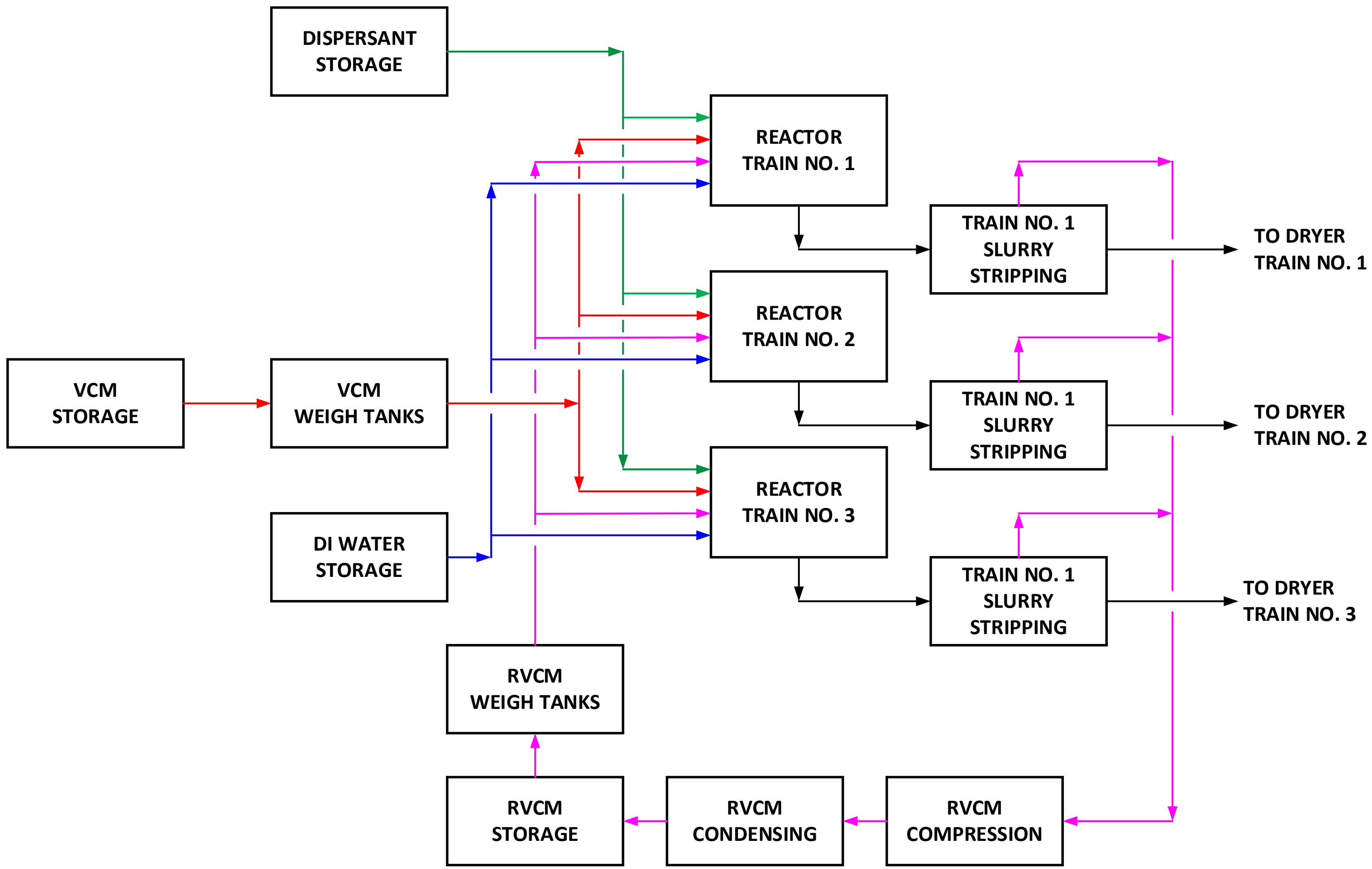
# Commercial PVC Technologies

- **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

# Suspension Process

- **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

# PVC Overview



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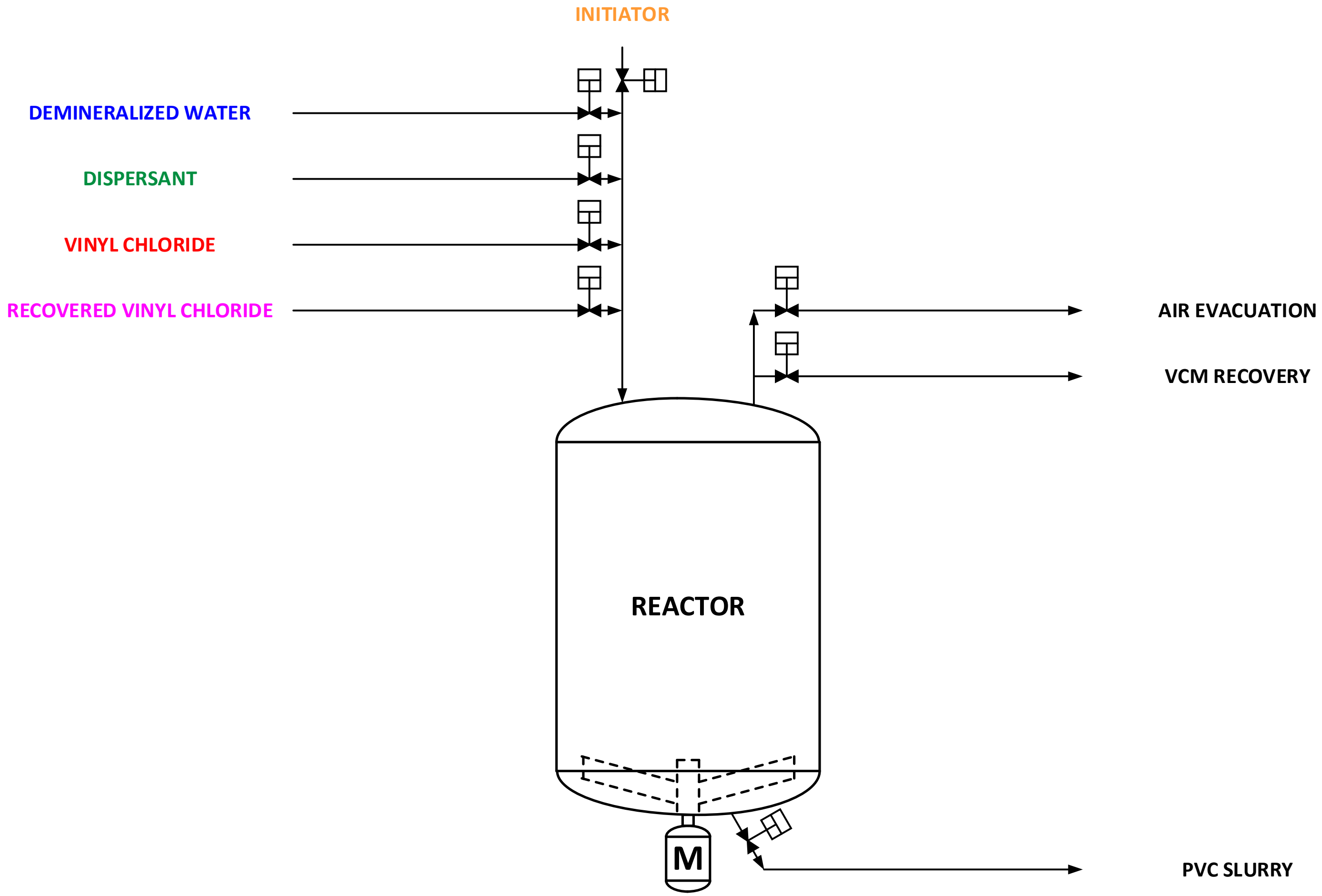
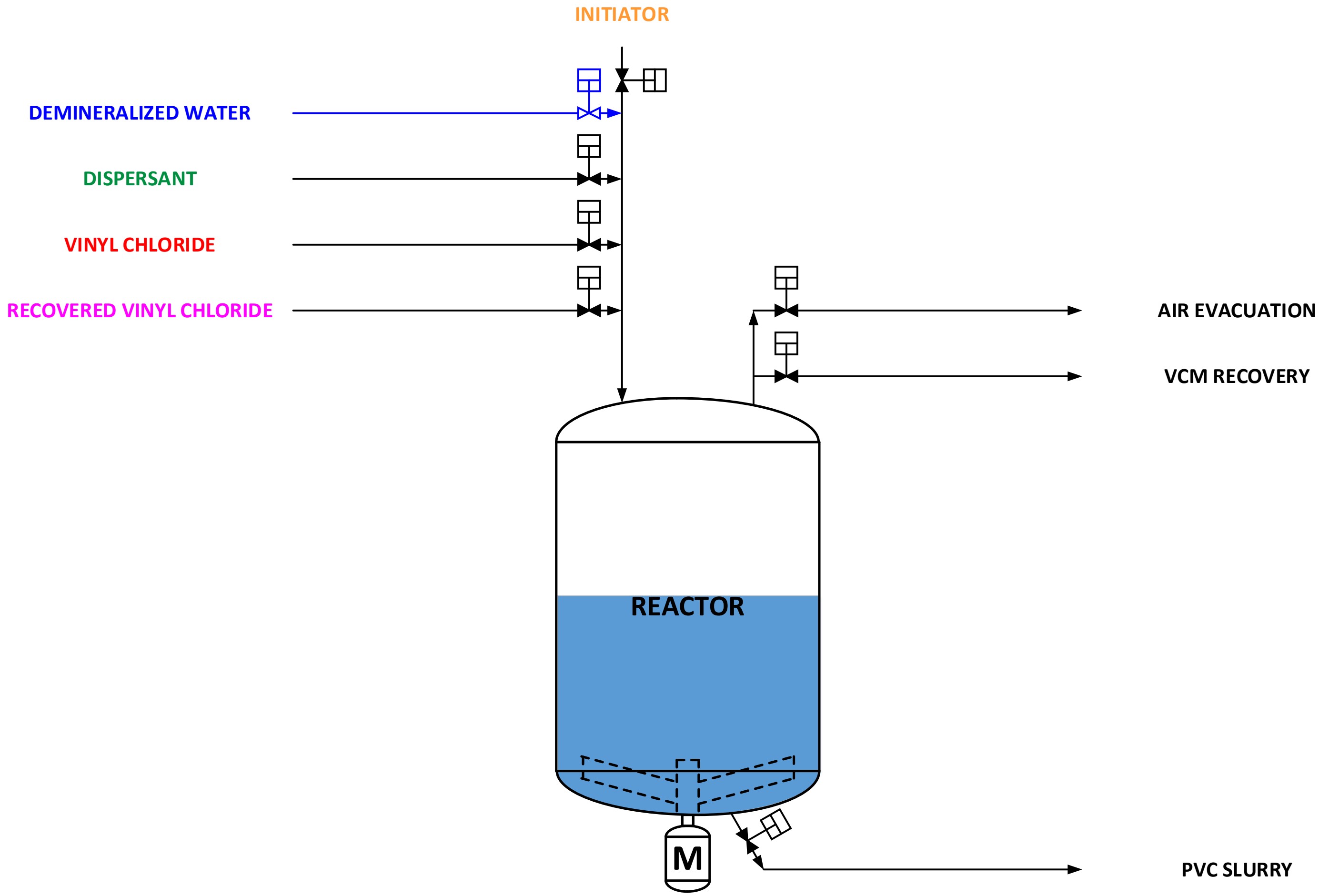
# Typical Reactor Cycle Time

| Reactor Step | Minutes | Hours |
|---|---|---|
| Charge / Heat Up | 45 | 0.75 |
| Reaction | 165 | 2.67 |
| Pressure Drop | 30 | 0.50 |
| Blowdown / Recovery / Wash | 60 | 1.00 |
| **Total** | 300 | 5.00 |

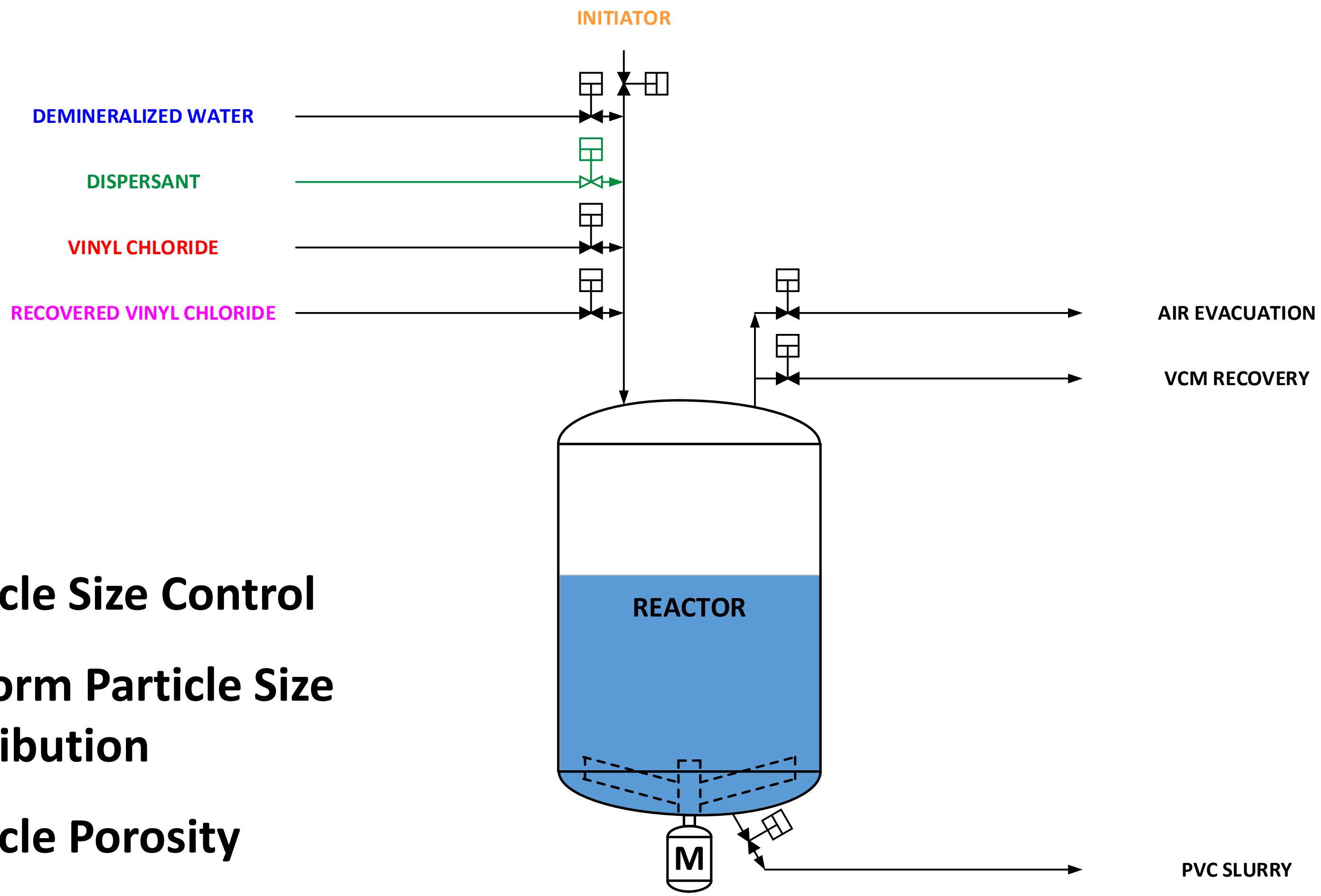
# PVC Reactor


INITIATOR
DEMINERALIZED WATER
DISPERSANT
VINYL CHLORIDE
RECOVERED VINYL CHLORIDE
AIR EVACUATION
VCM RECOVERY
REACTOR
M
PVC SLURRY

# Demineralized Water

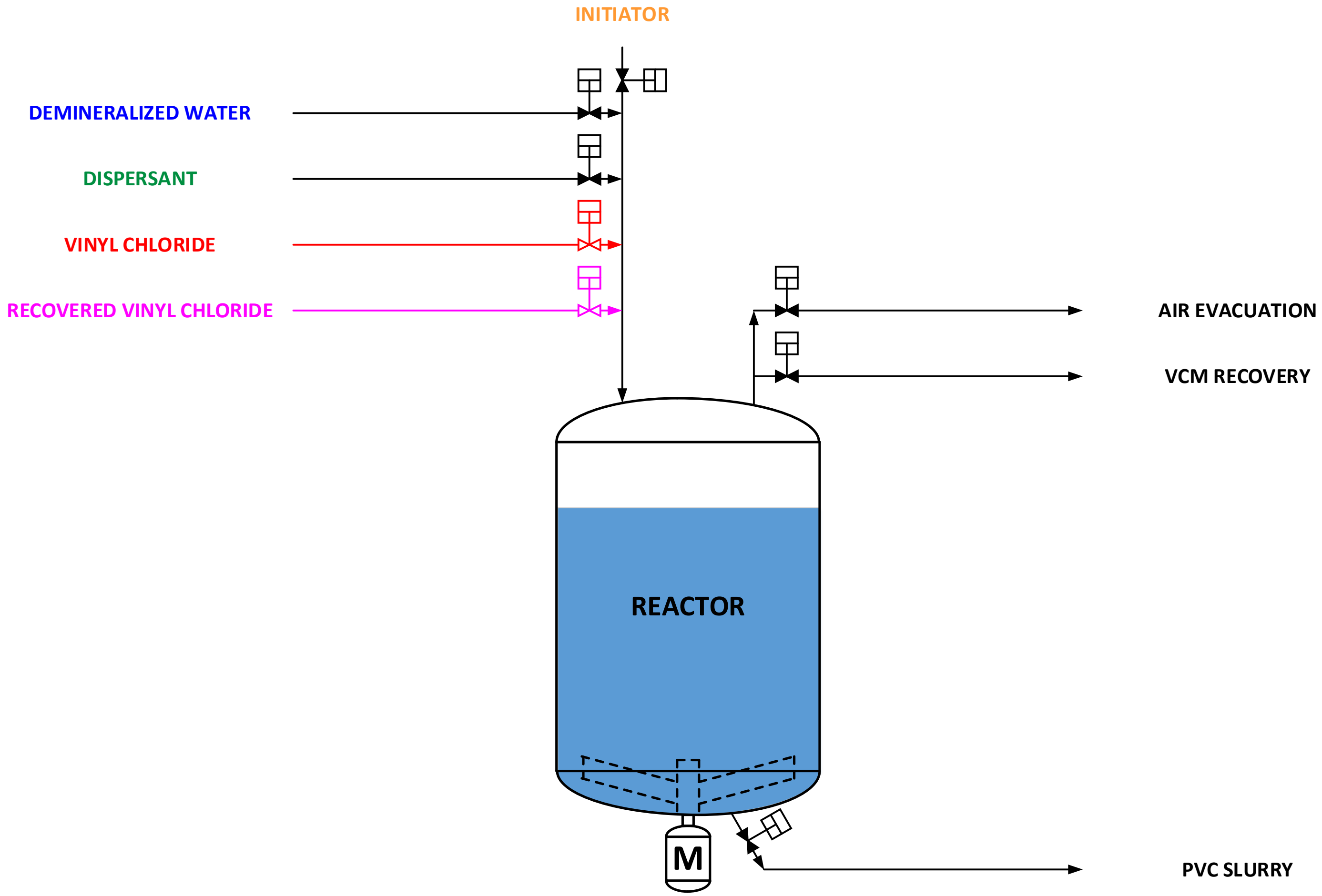


# Dispersant

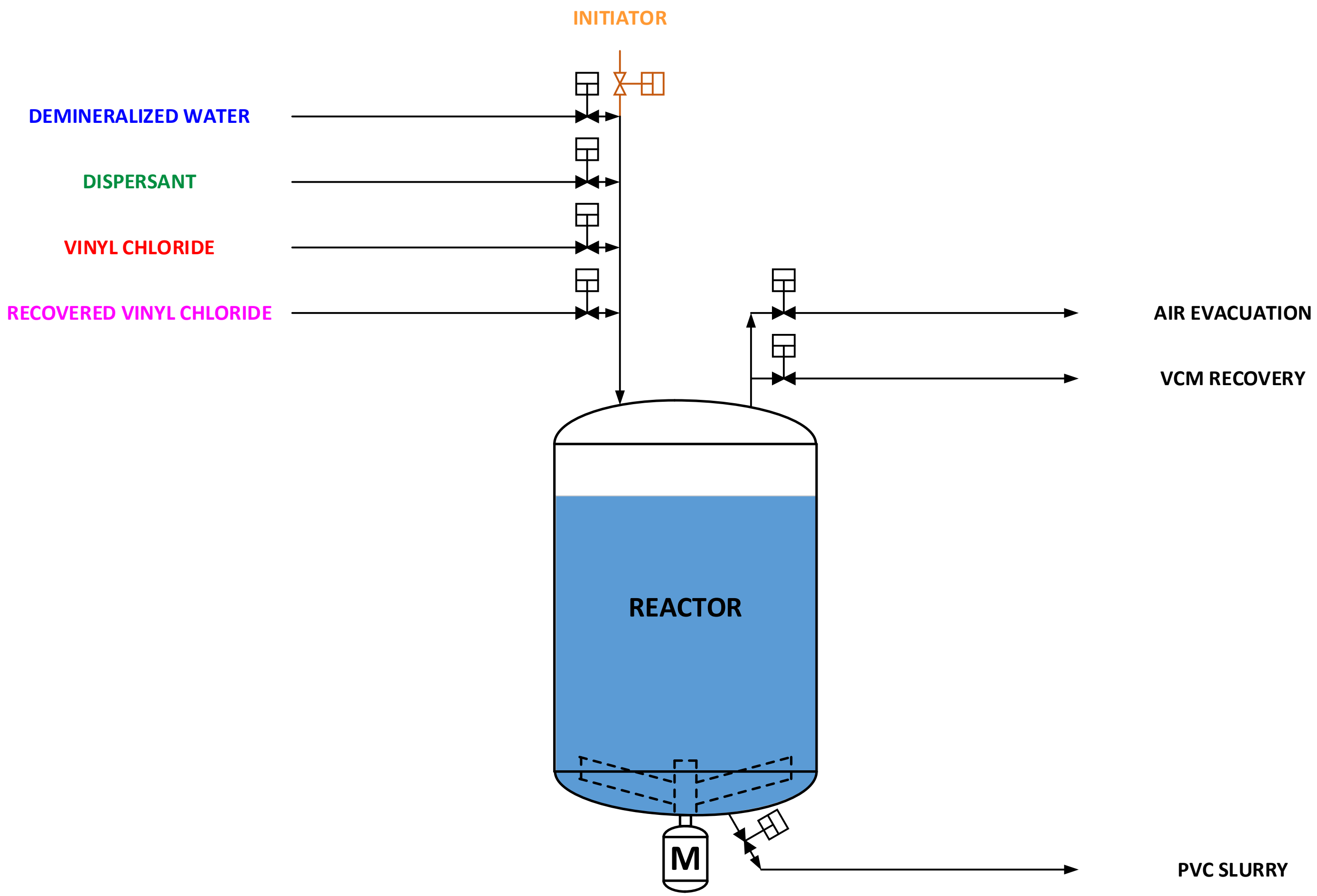



- **Particle Size Control**
- **Uniform Particle Size Distribution**
- **Particle Porosity**

# Vinyl Chloride



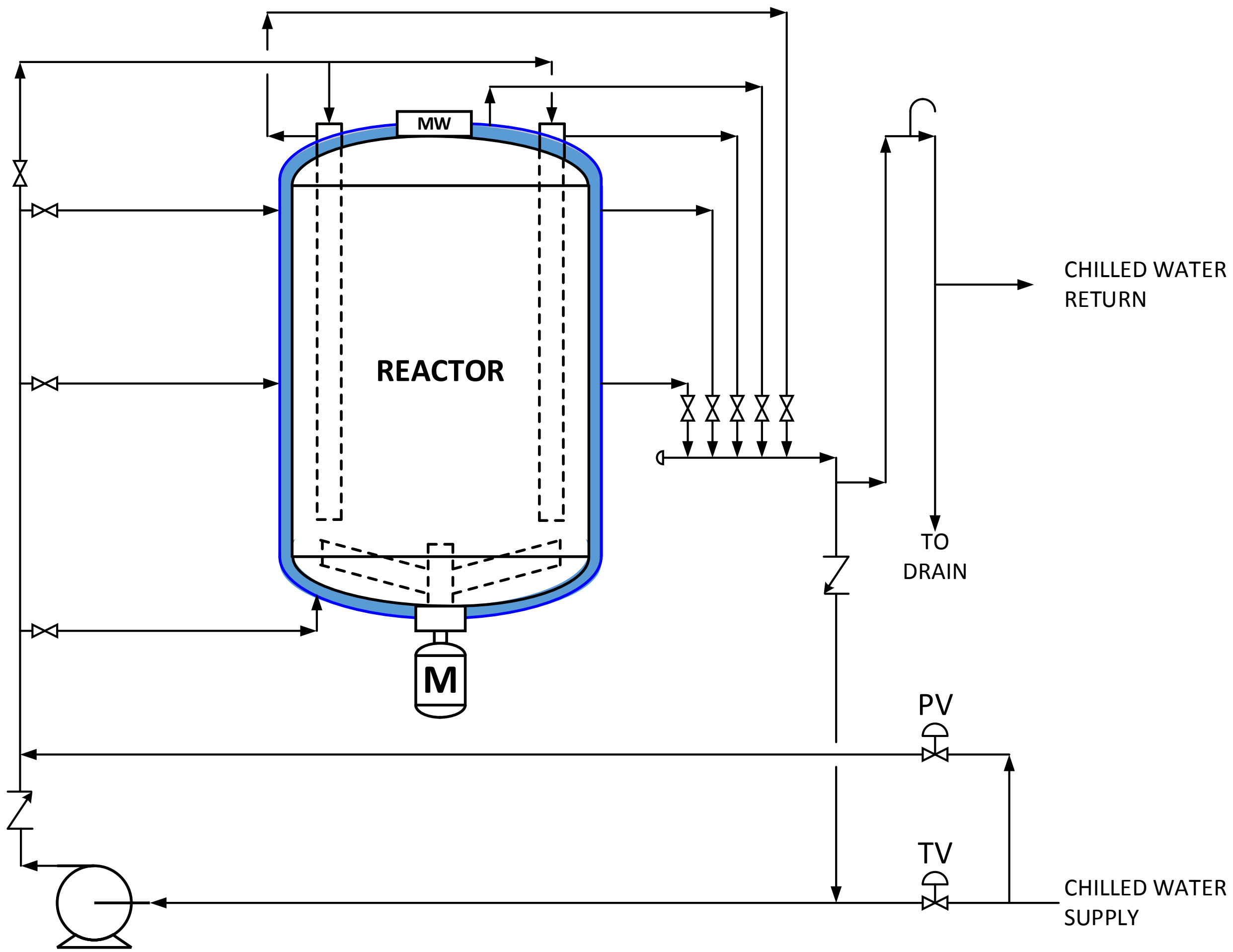
# Initiator


INITIATOR
DEMINERALIZED WATER
DISPERSANT
VINYL CHLORIDE
RECOVERED VINYL CHLORIDE
AIR EVACUATION
VCM RECOVERY
REACTOR
M
PVC SLURRY

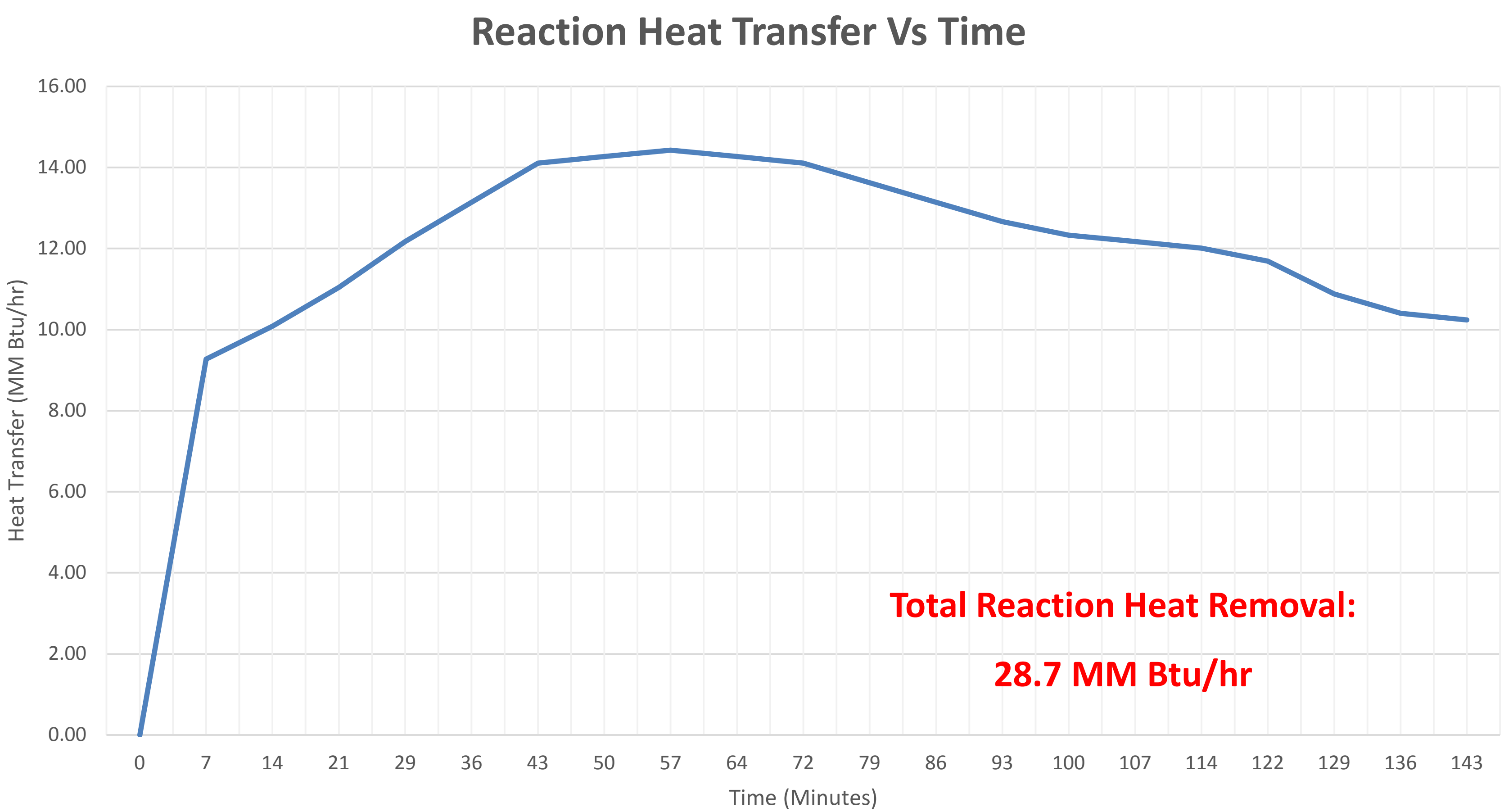
# Increasing PVC Production

| Change | Purpose |
|---|---|
| Reactor Size | Larger Batches |
| Closed Mode Operation | Minimize Reactor Openings / Process Steps |
| External VCM Removal | Reduce Reactor Cycle Time / Continuous Slurry Stripping |
| Preheating Demin Water | Reduce Reactor Cycle Time |
| Clean Wall Technology | Reduce Reactor Cleaning Frequency / Increase Uptime |

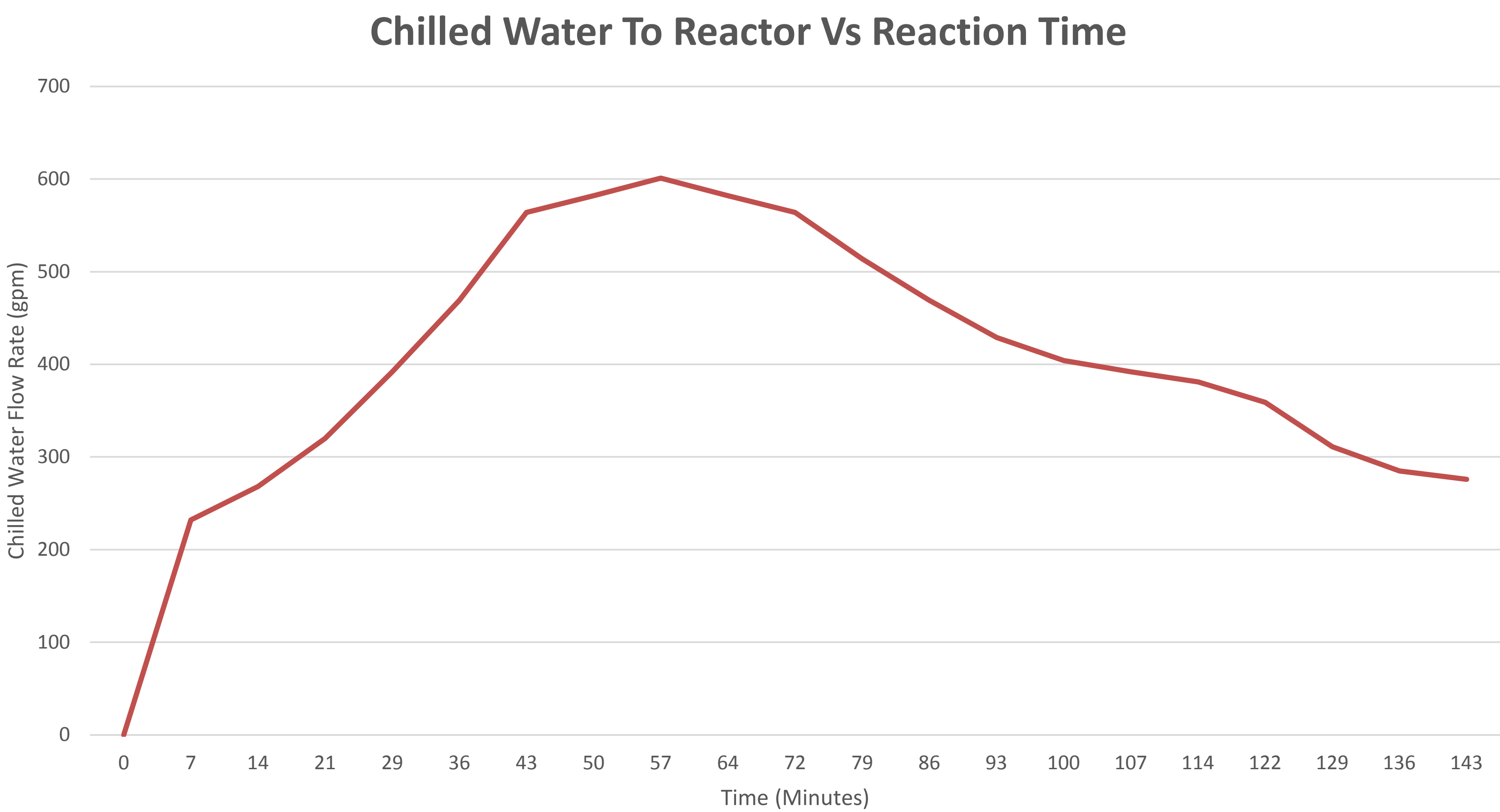
# Jacket Cooling



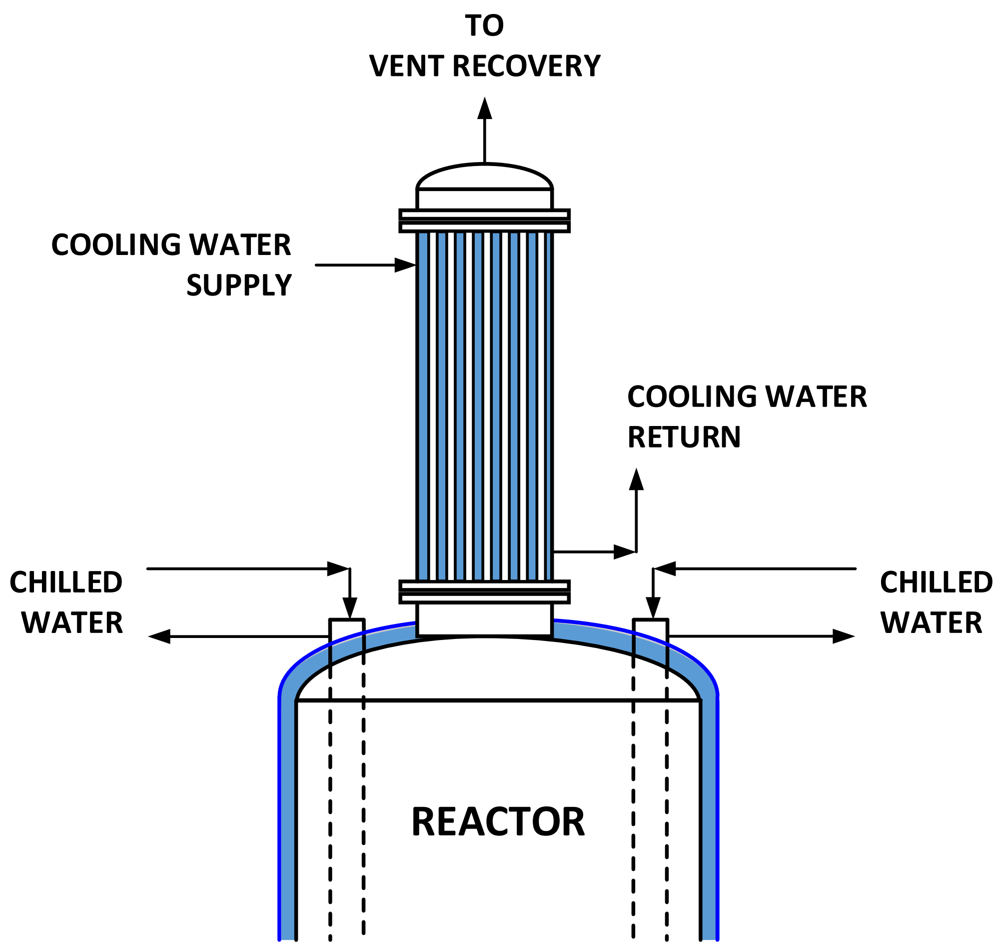
# Heat Transfer



# Chilled Water Makeup



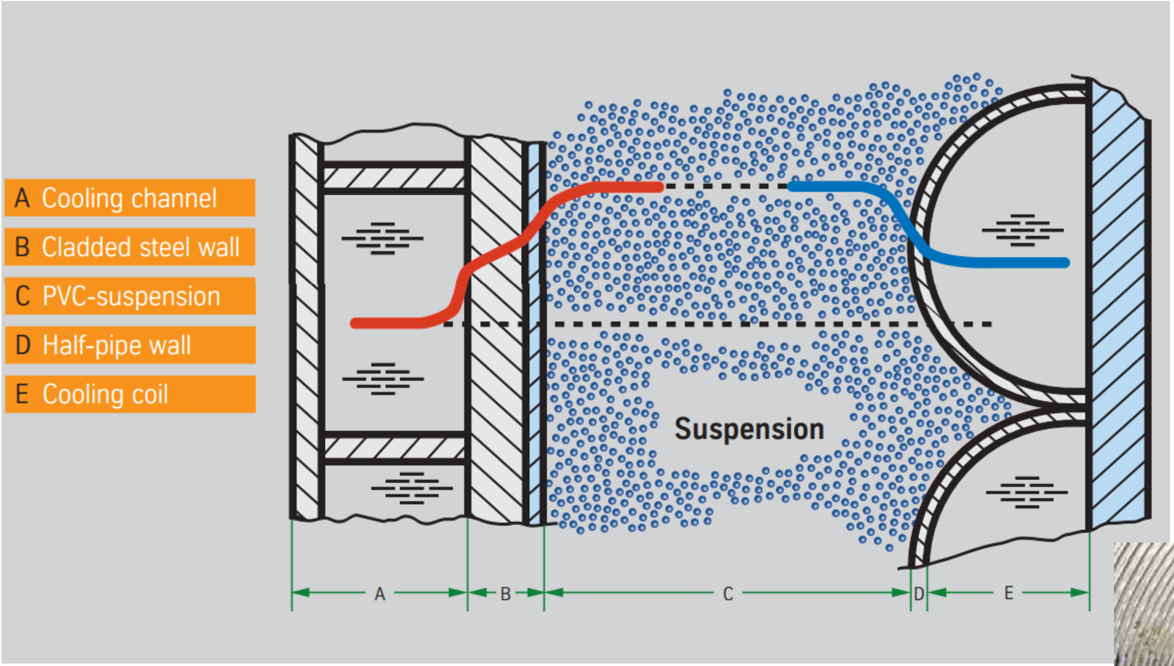
# Vent Condenser

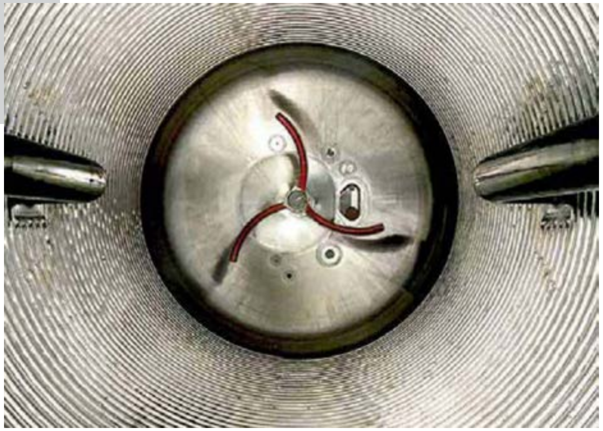


# Vinnolit High-Performance Reactor

**Conventional Reactor**

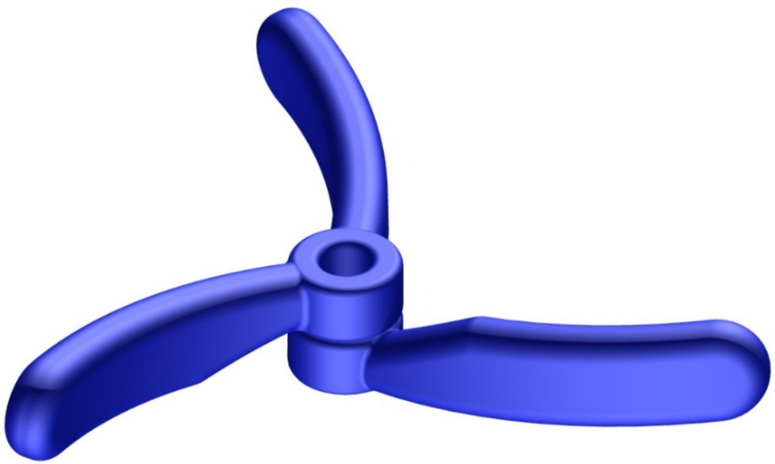
**High-Performance Reactor**



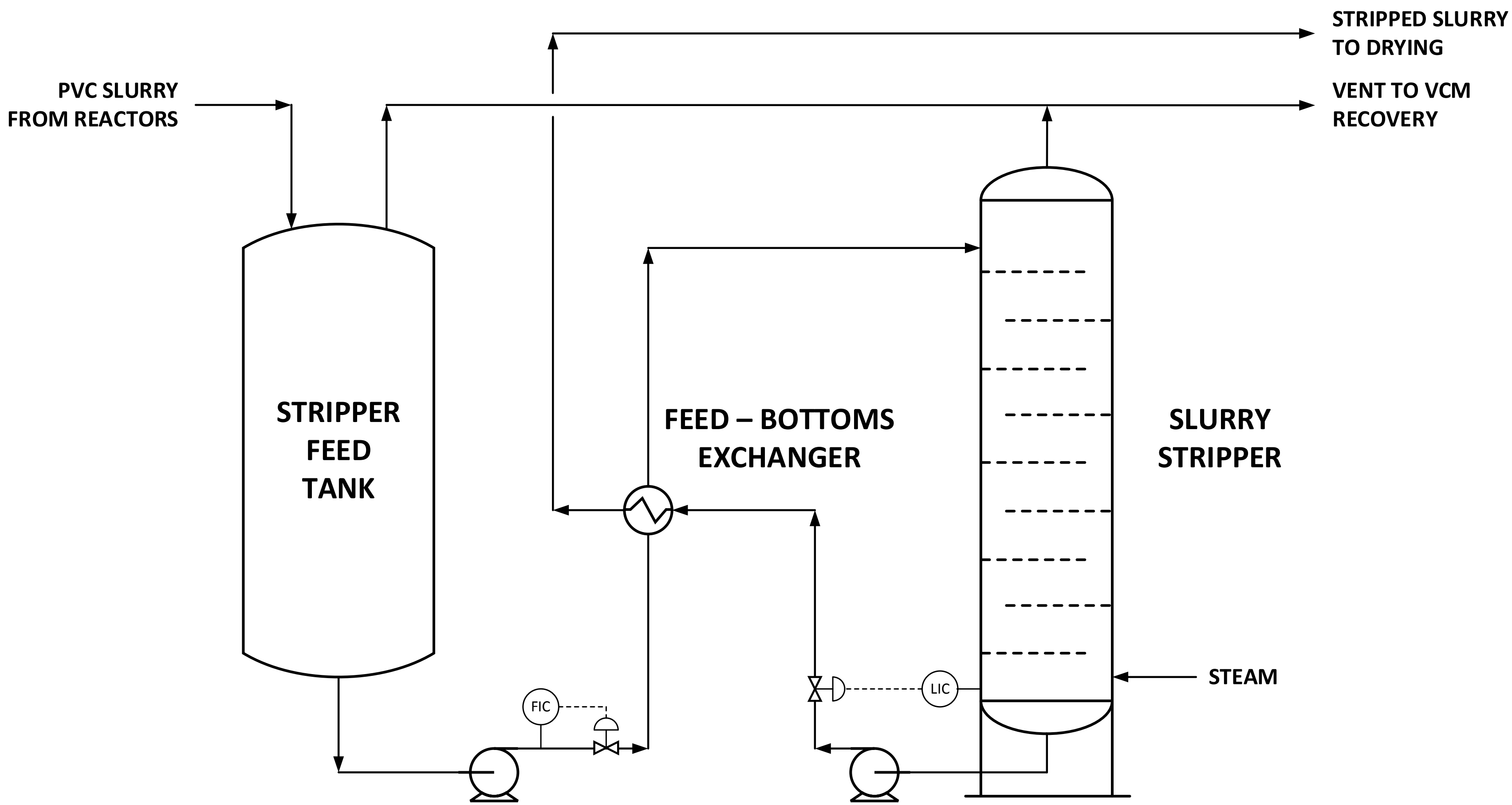
# Reactor Agitator Impeller

**Pfaudler RCI Agitator Impeller**

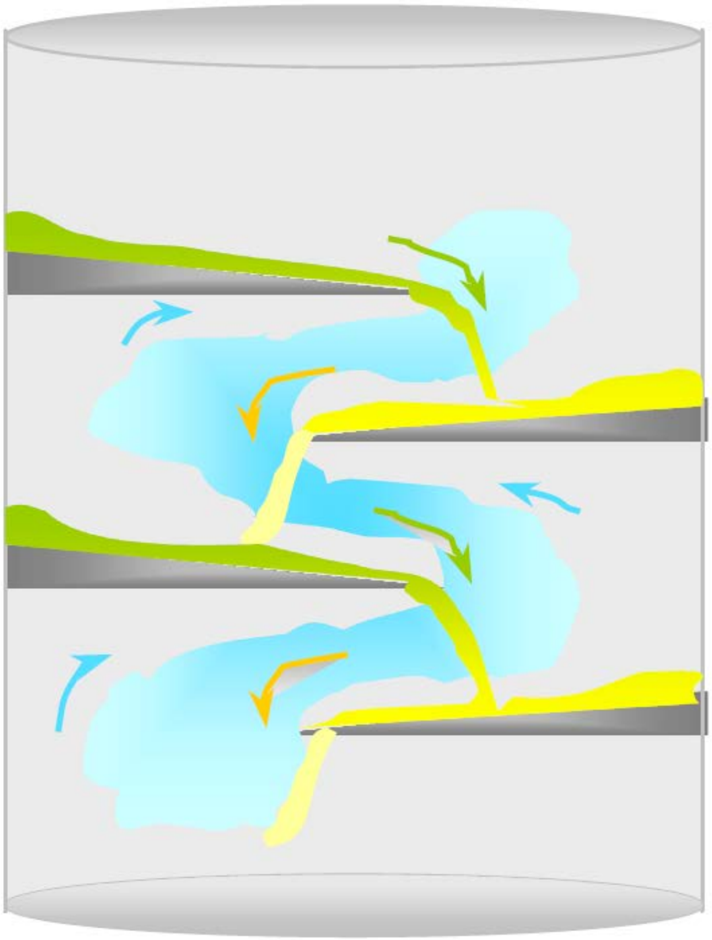


- **Radial Design**
- **High Shear (Low Efficiency)**
- **Poor Pumping**
- **Long History With PVC Reactors**

# Slurry Stripping



# Baffle Trays

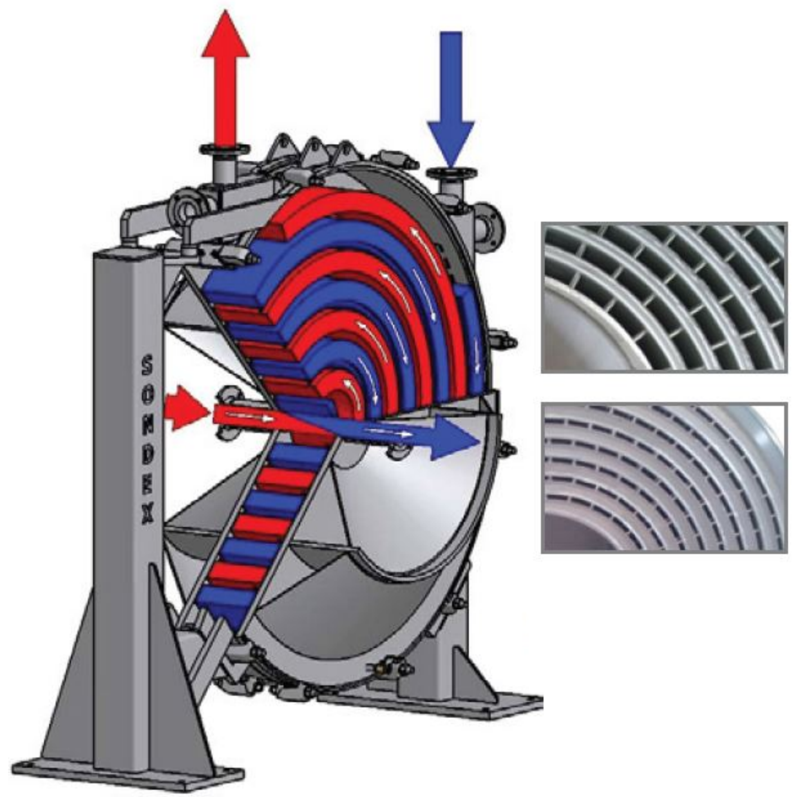


**Low Pressure Drop**

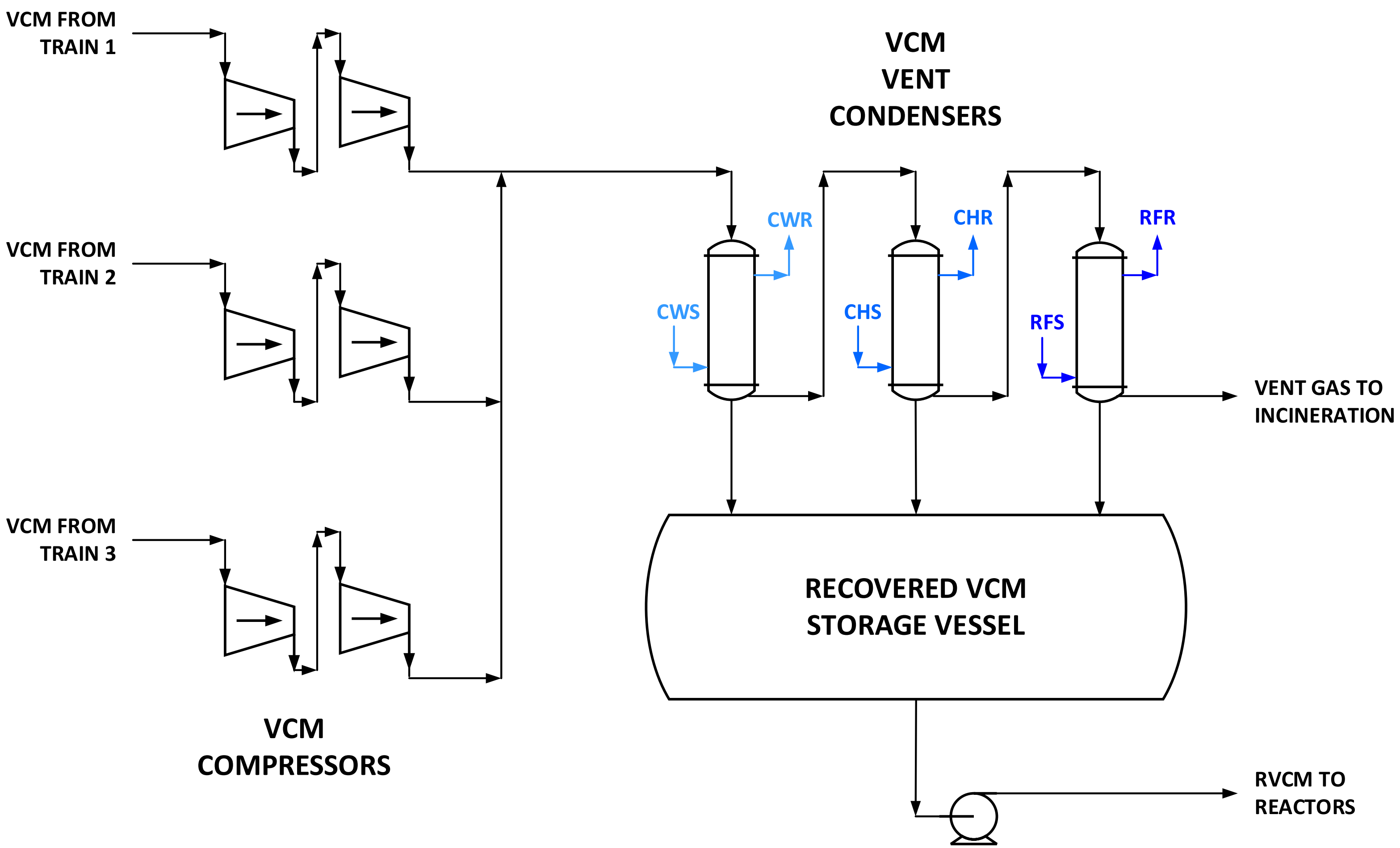
**Low Fouling**

**Low Efficiency**

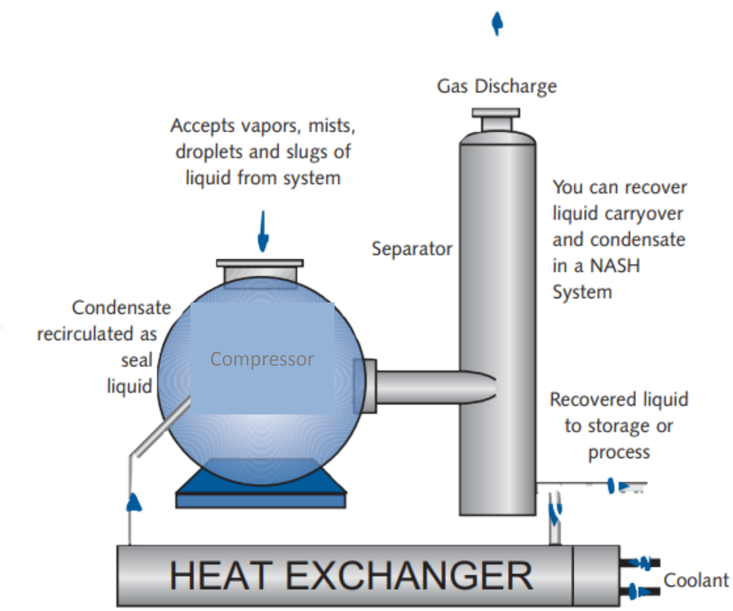
# Spiral Heat Exchanger

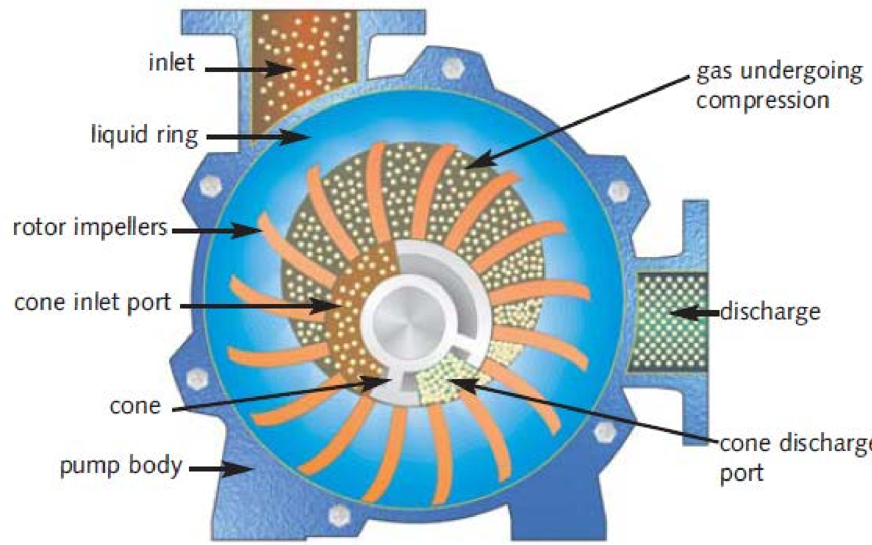


# VCM Recovery



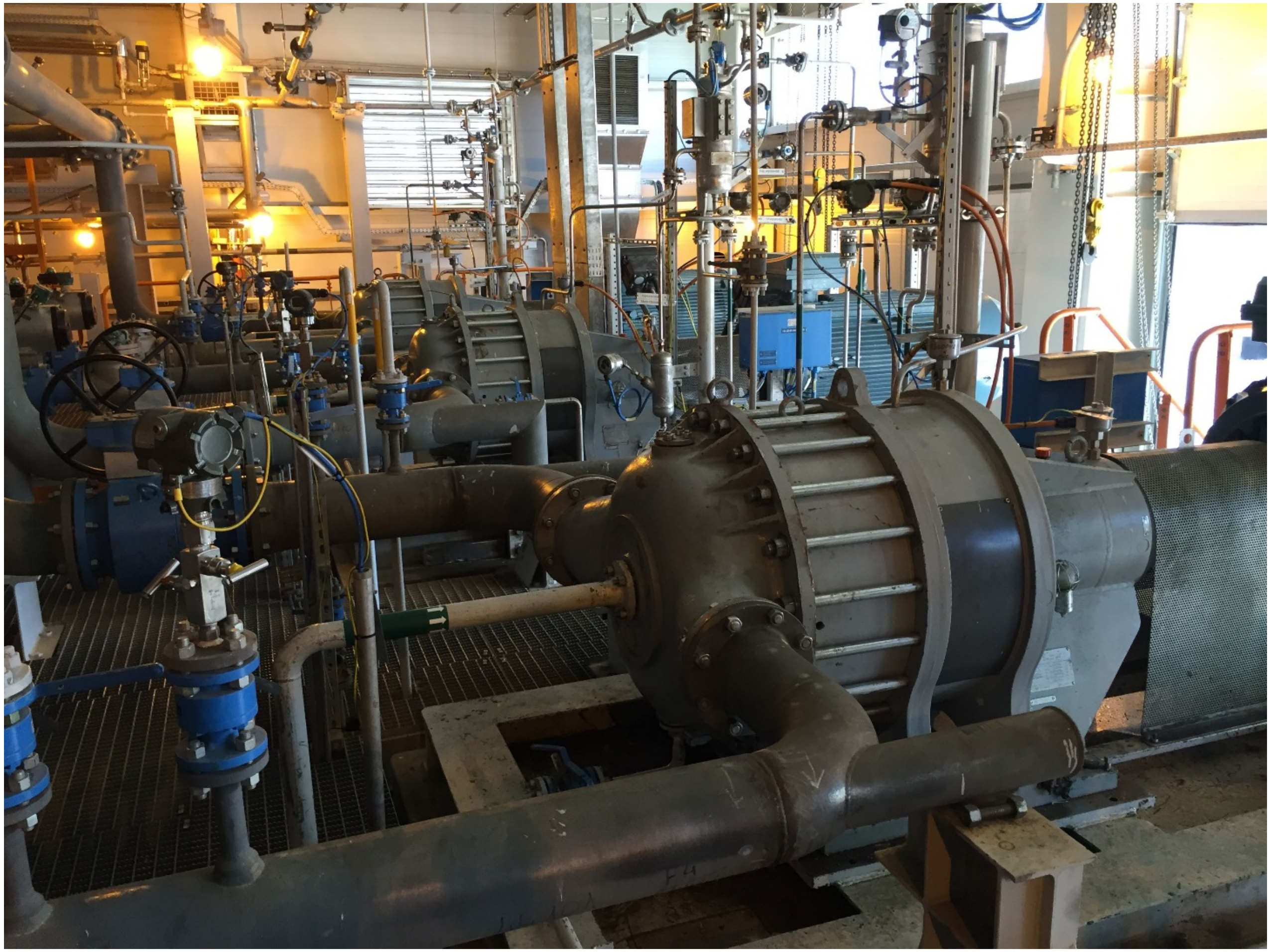
# Liquid Ring Compressors



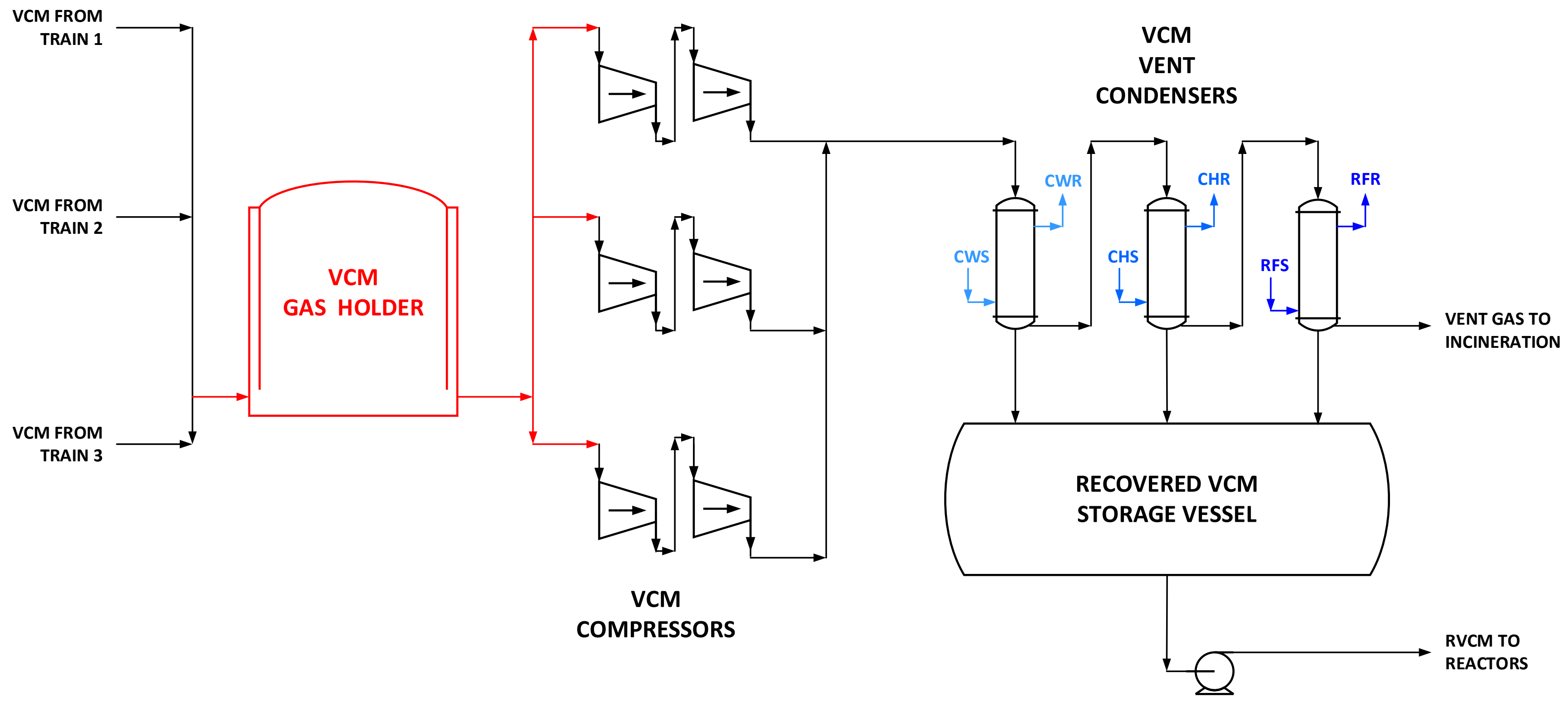

Gardner Denver Nash

# VCM Recovery Compressors

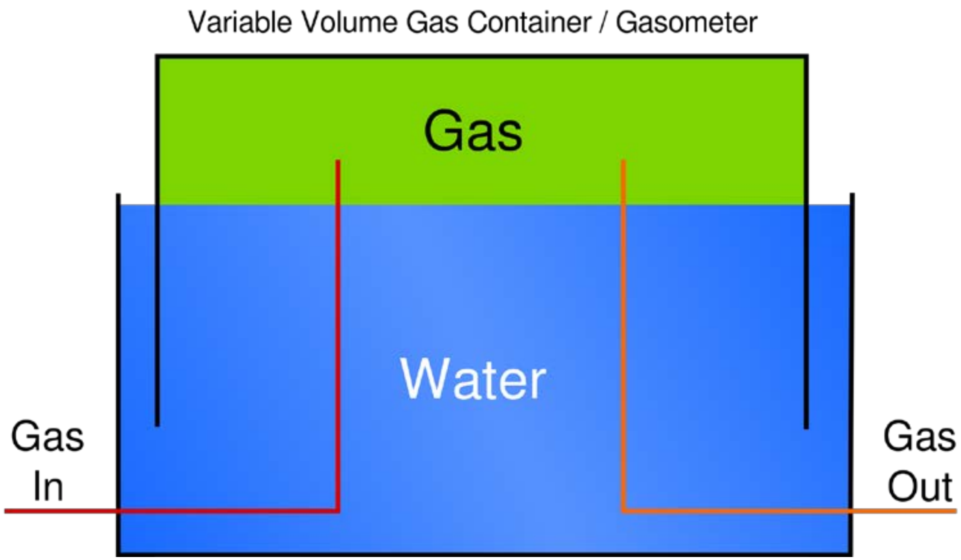


Gardner Denver Nash

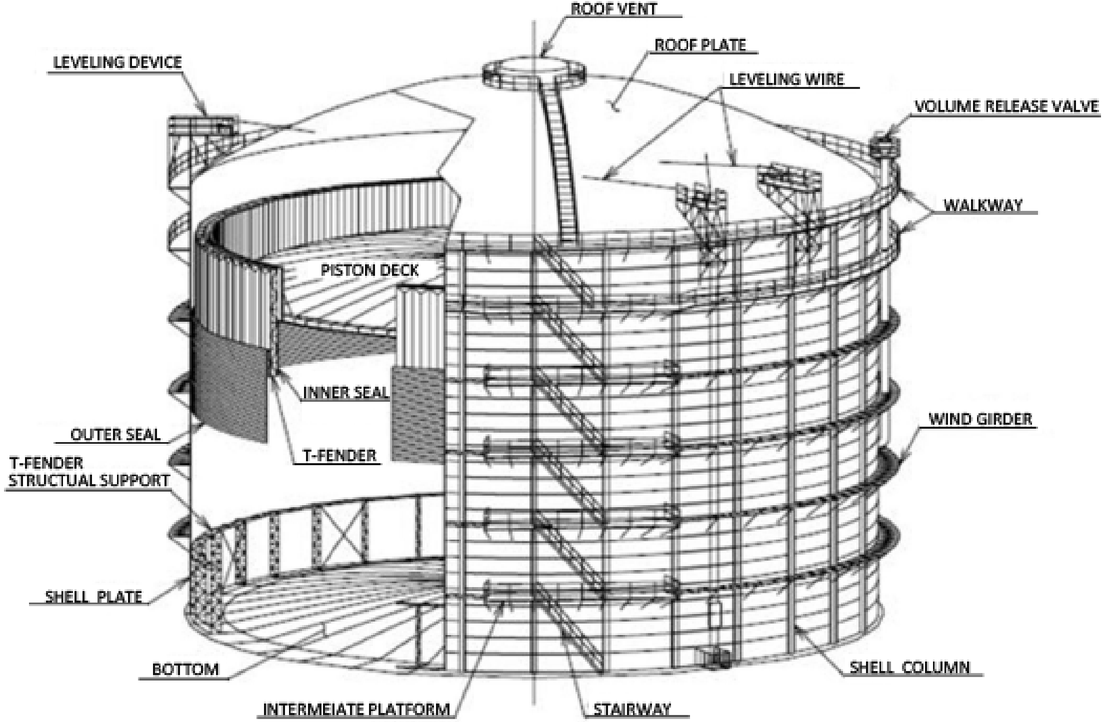
# VCM Gas Holder



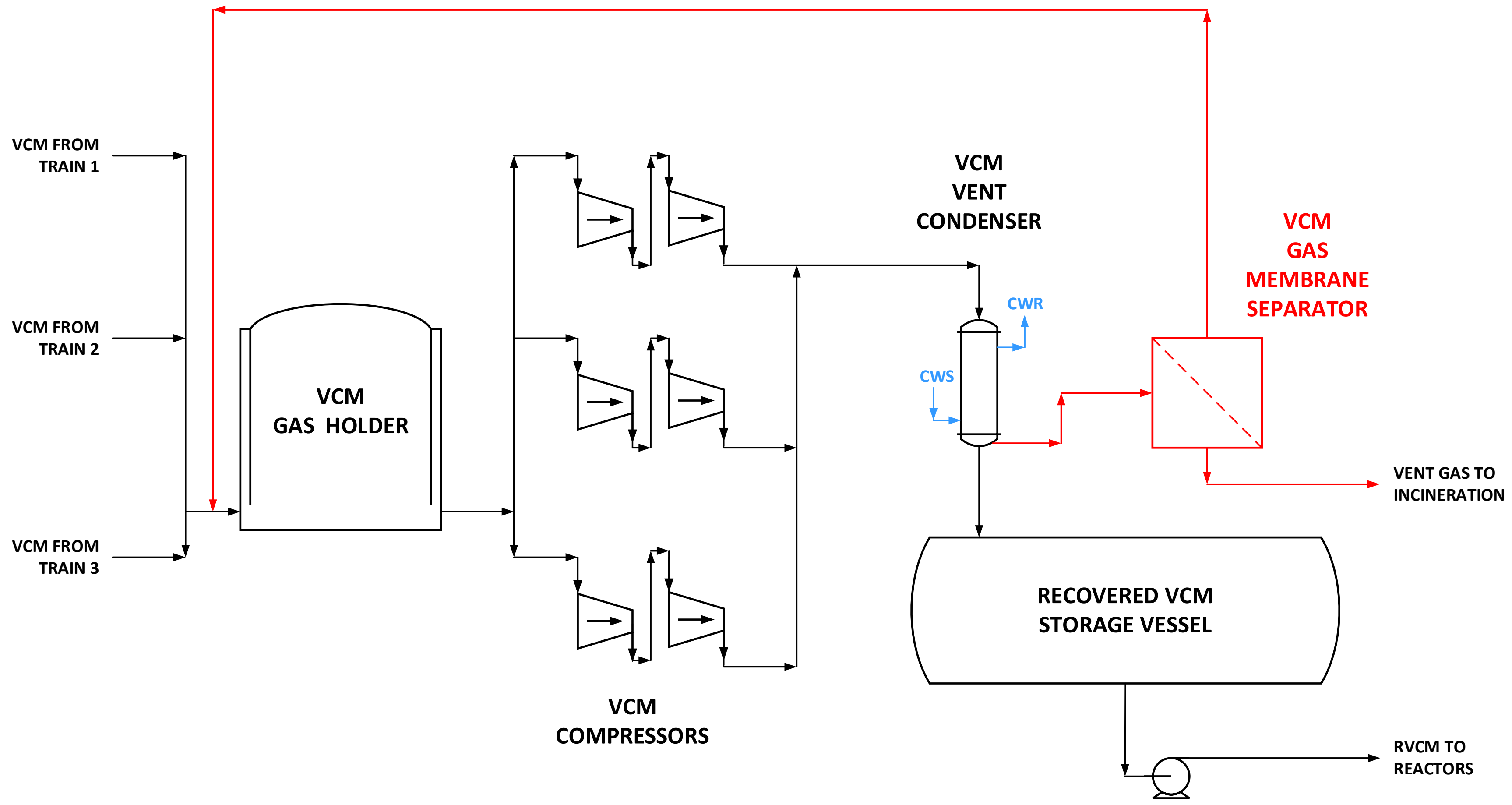
# Wet-Seal Gas Holder

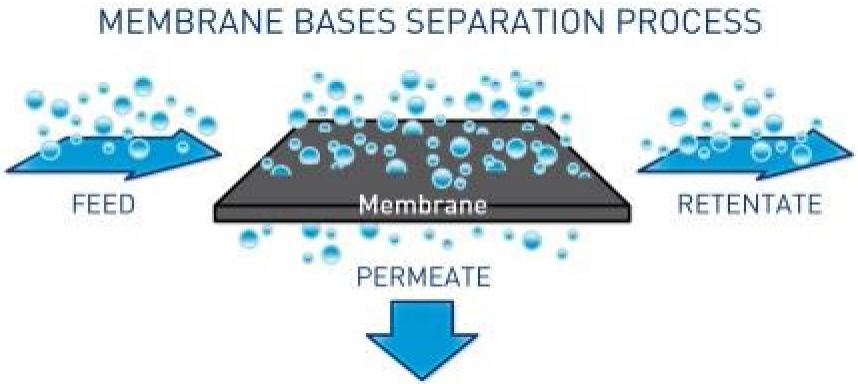
# Dry-Seal Gas Holder



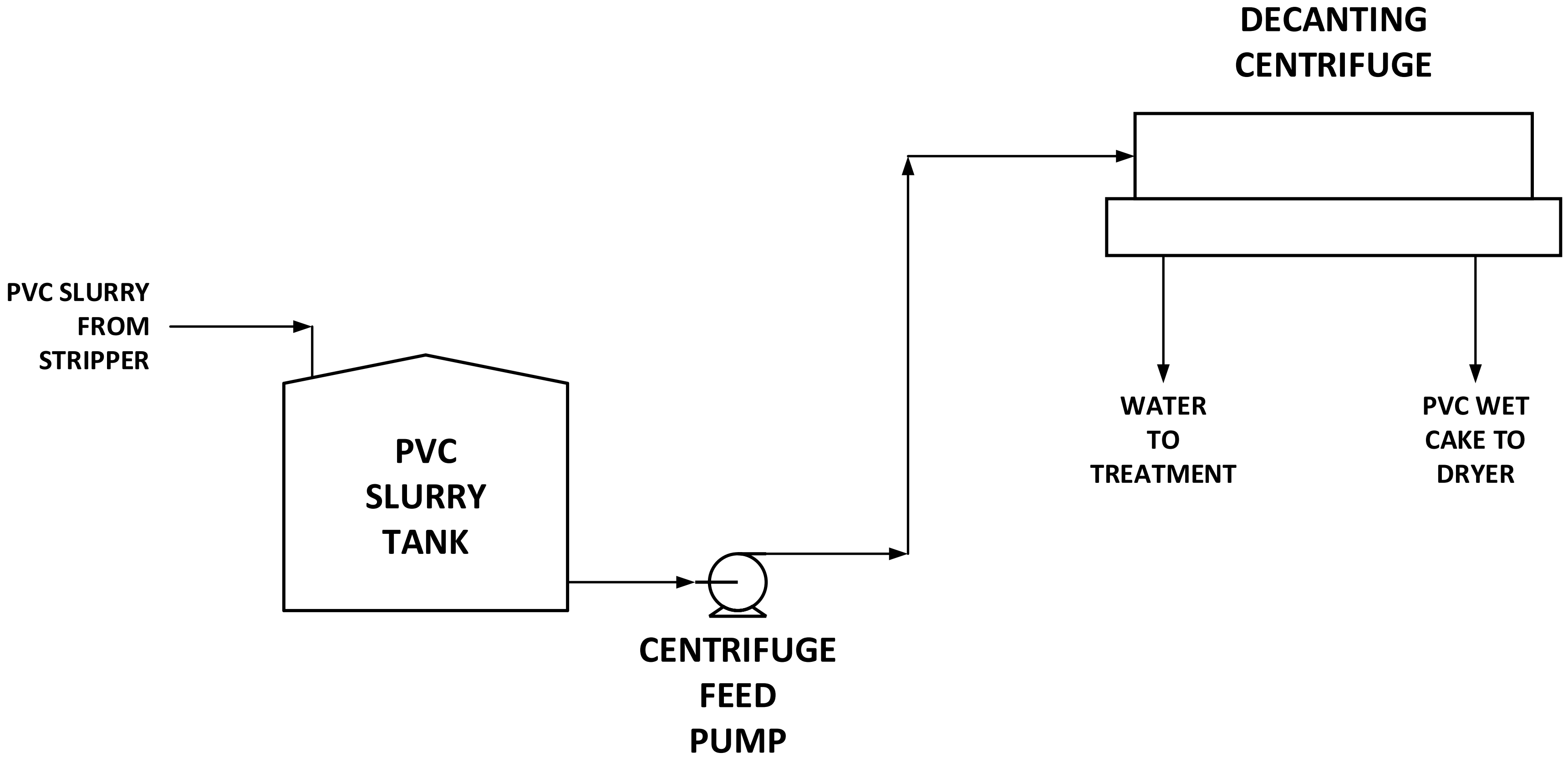
# Membrane Separation



# Membrane Separator

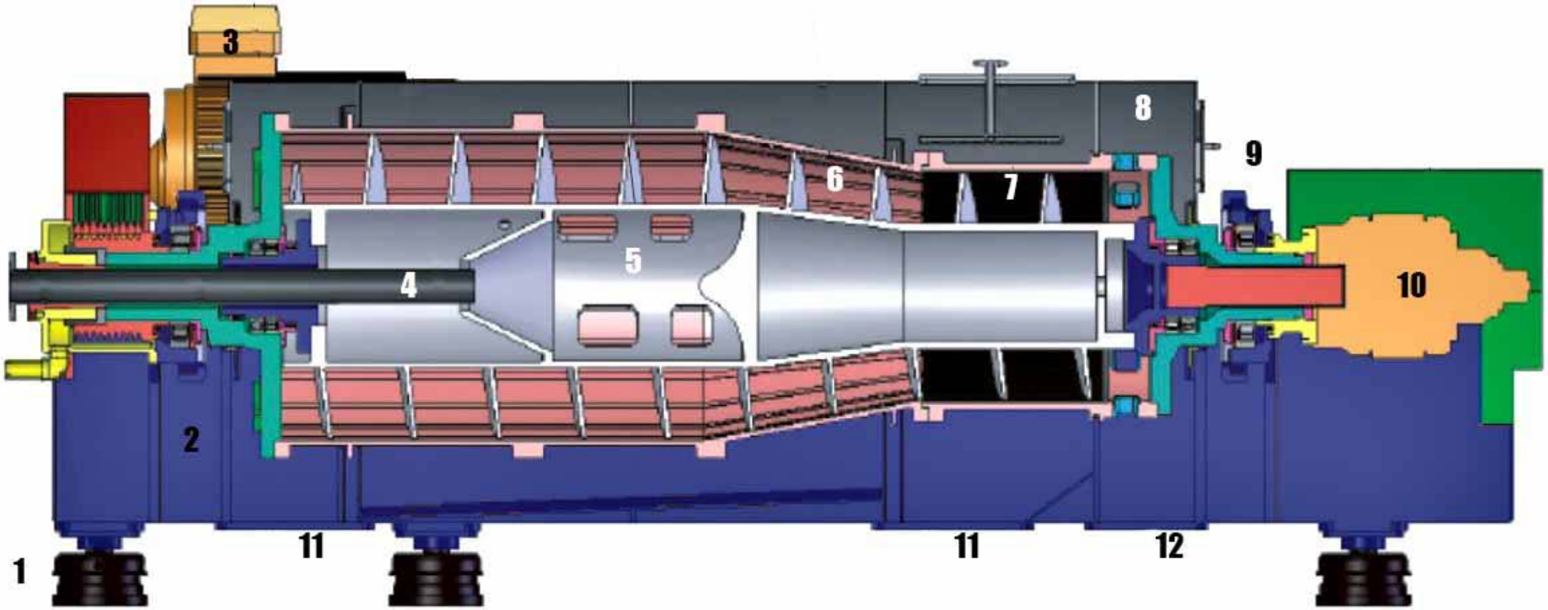


# PVC Dewatering

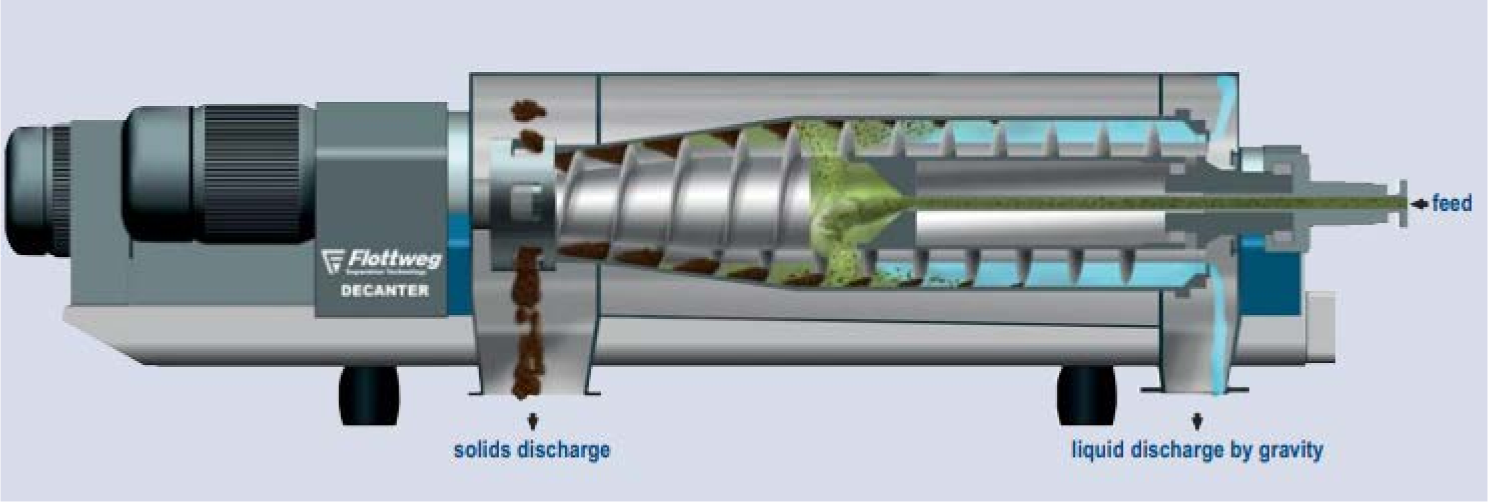


# Decanting Centrifuge

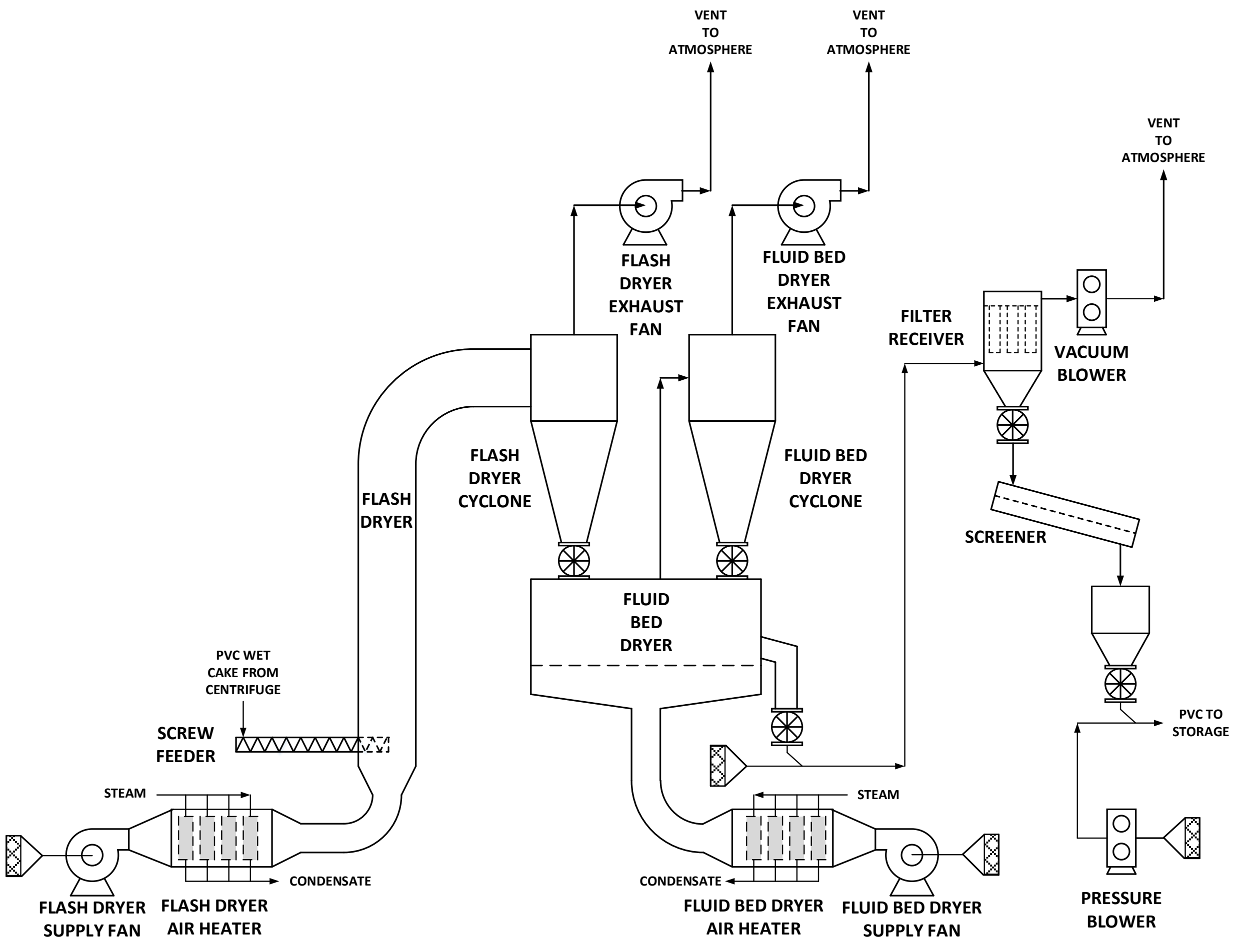
1. VIBRATION ABSORBER
2. BASE
3. MAIN MOTOR
4. FEED TUBE
5. CONVEYOR
6. BOWL
7. SCREEN
8. COVER
9. BEARING SEAT
10. GEARBOX
11. LIQUIDS DISCHARGE
12. SOLIDS DISCHARGE



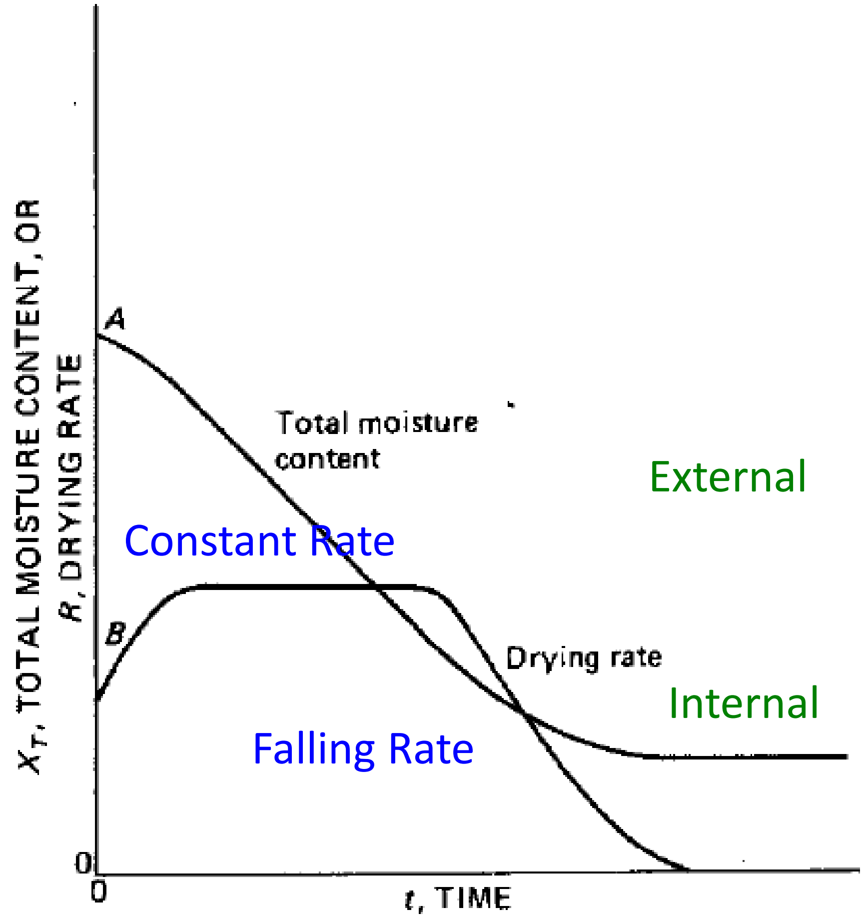
# Decanting Centrifuge




# FD-FB PVC Dryer

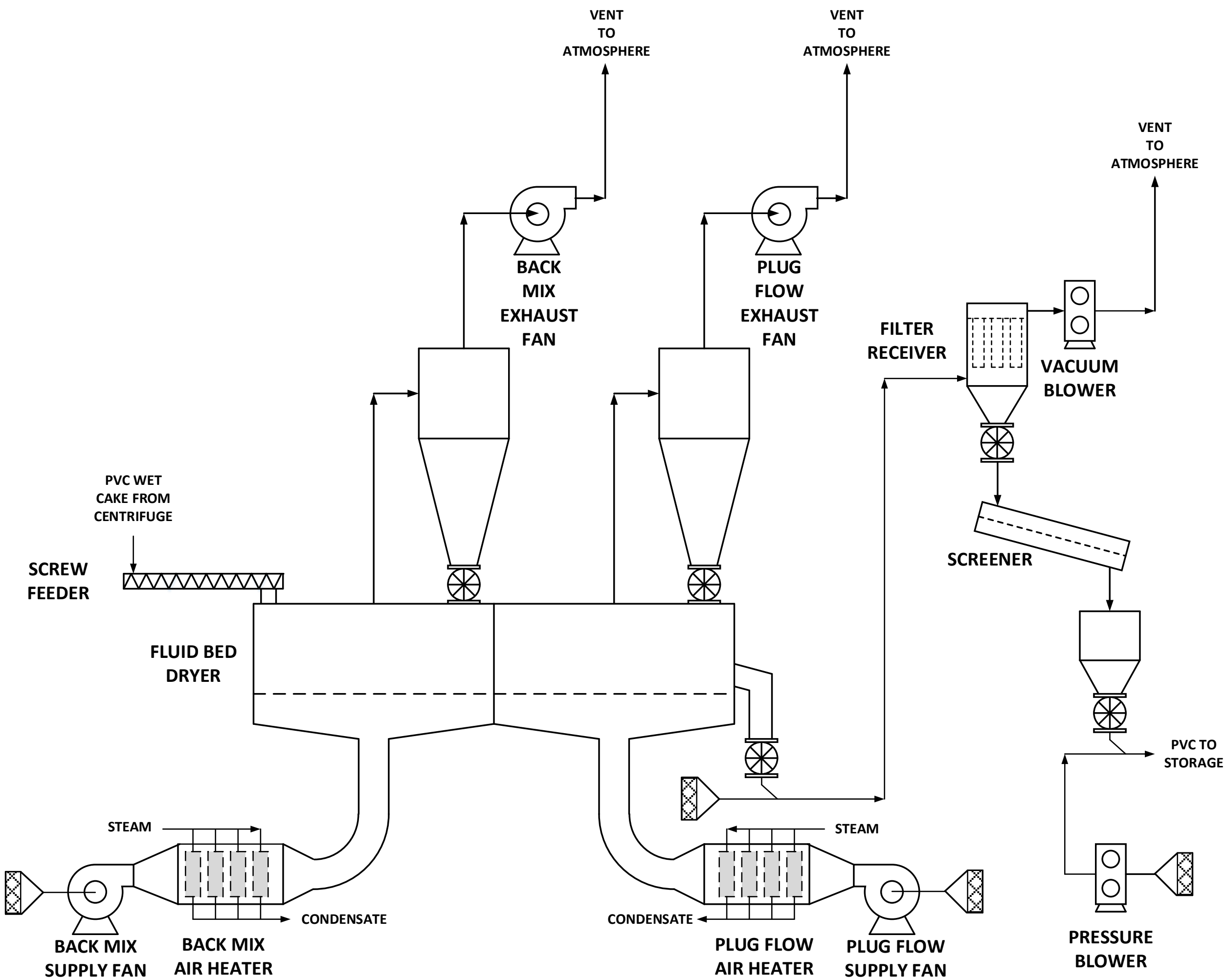


# Drying Curve

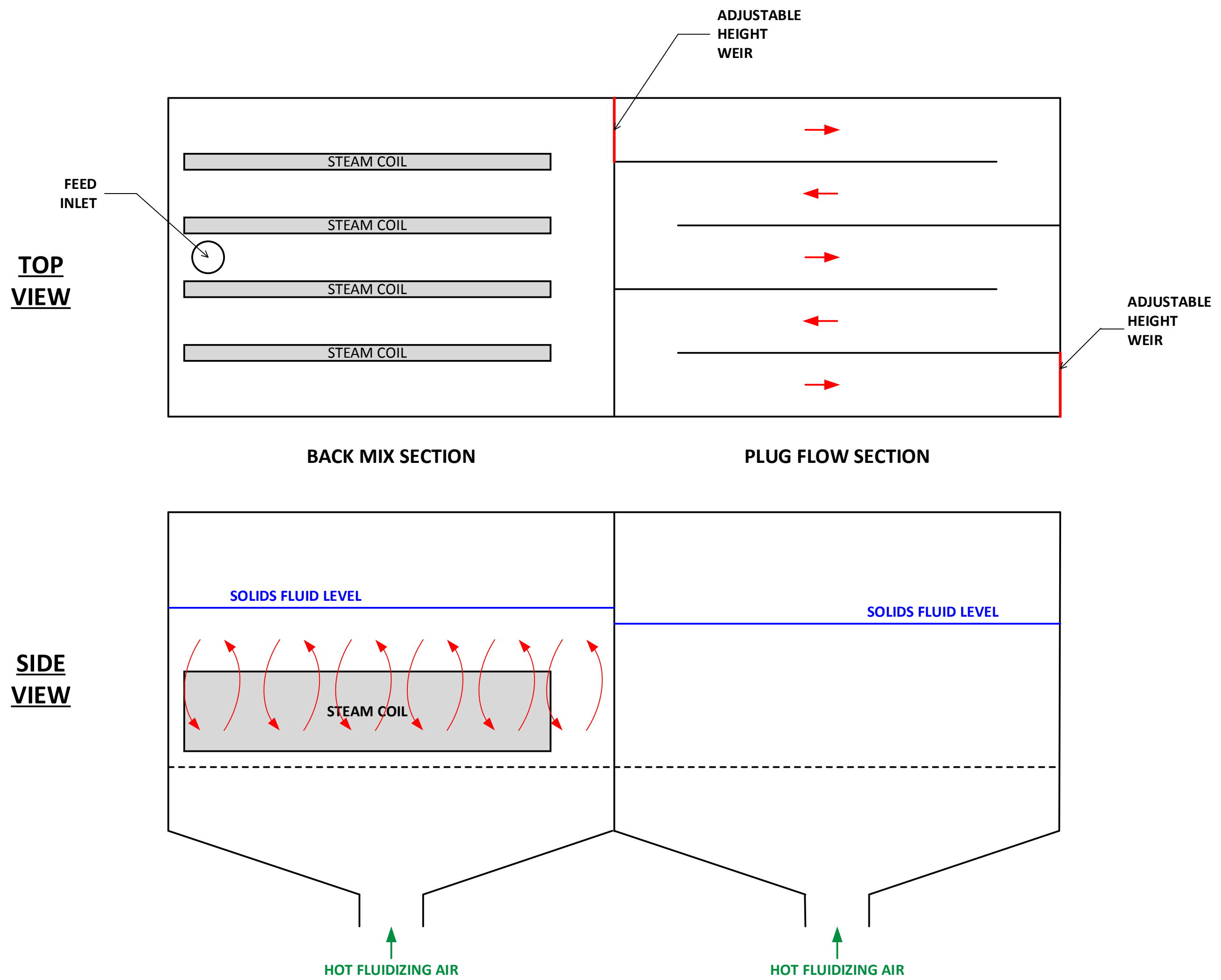



McCabe, 4th Ed., "Drying Of Solids"

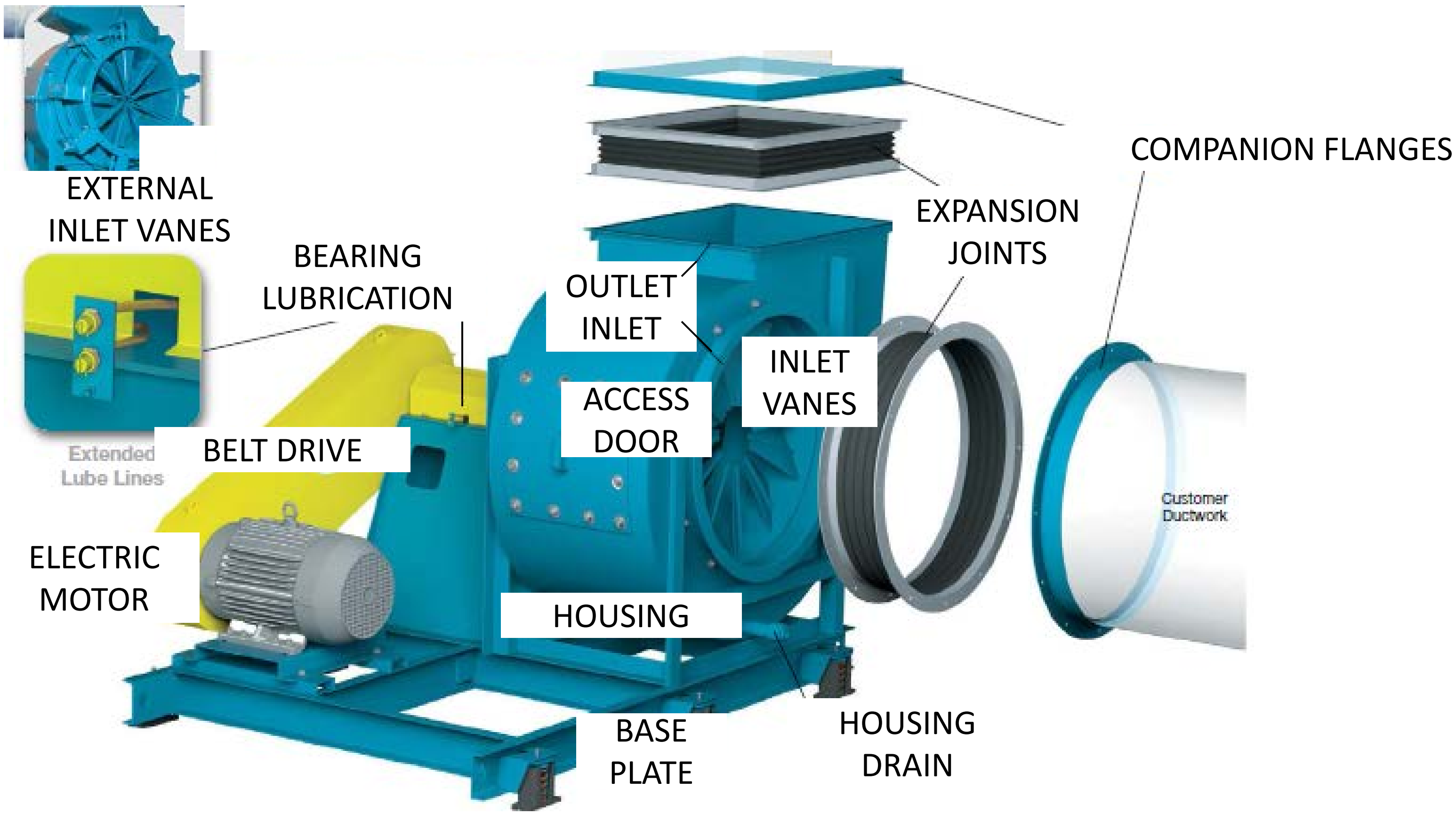
# BM – PF Fluid Bed Dryer



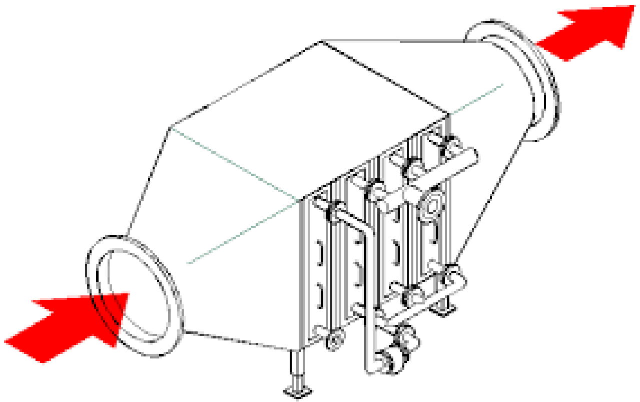
# BM – PF Fluid Bed Dryer

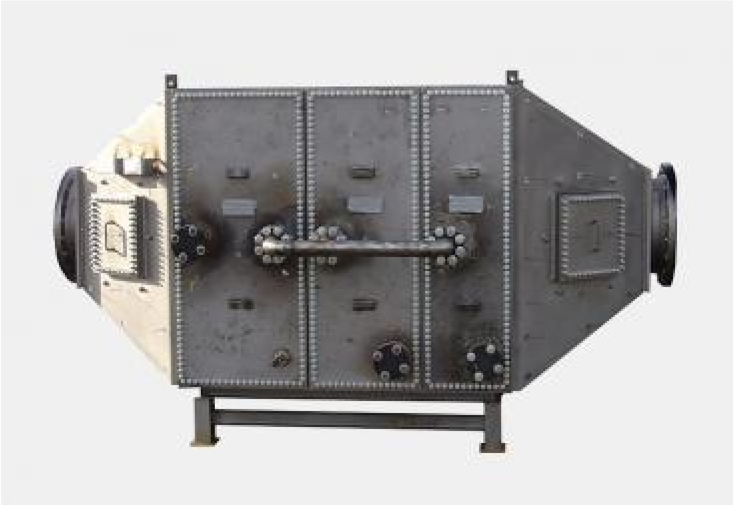


# Centrifugal Fan

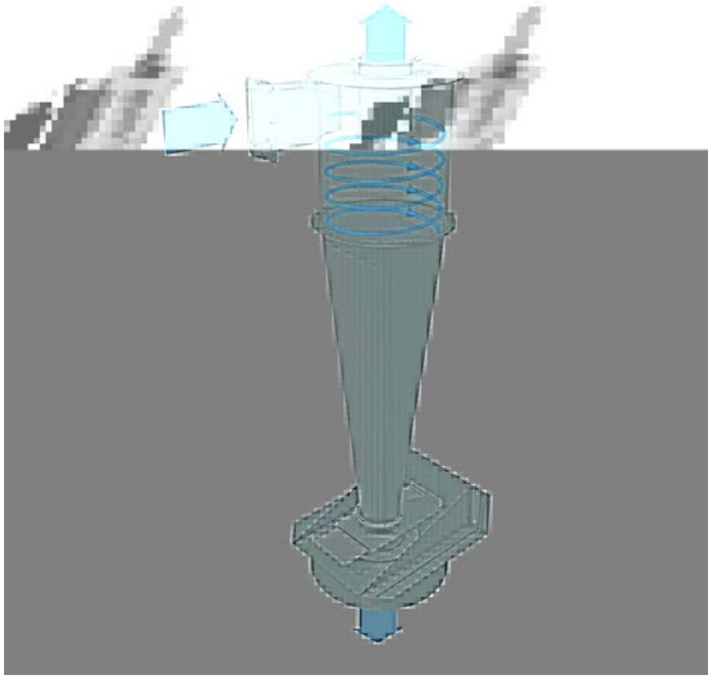


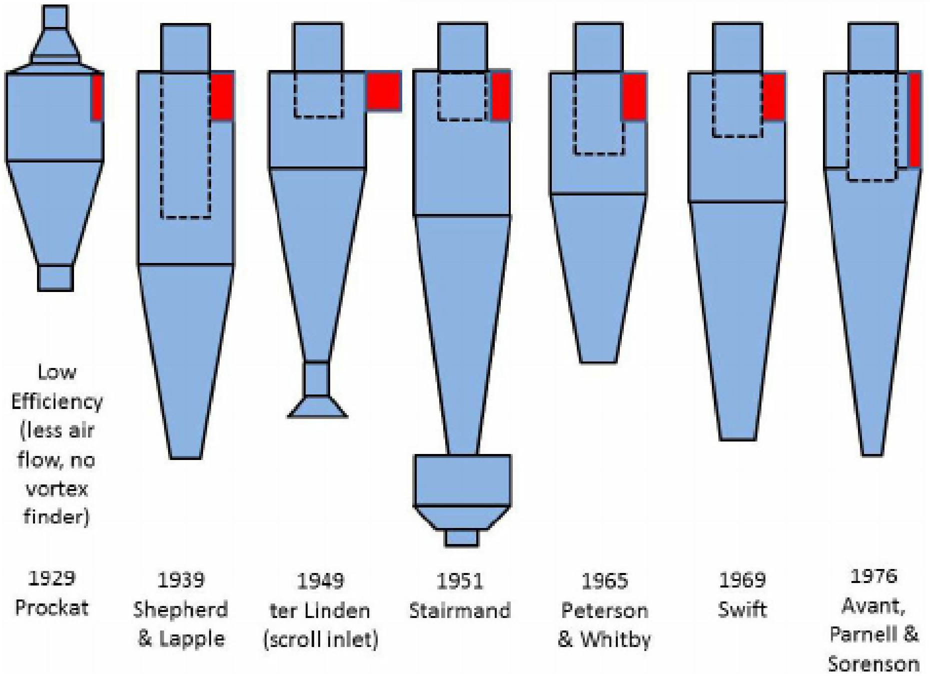
# Air Heater



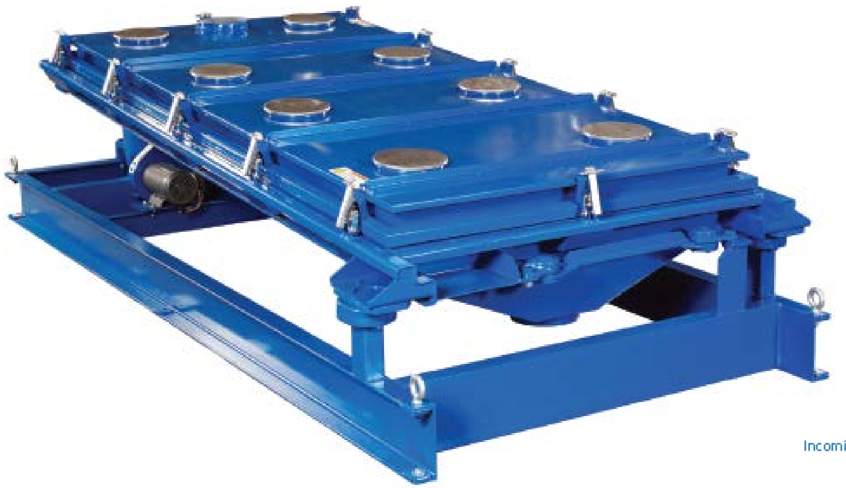


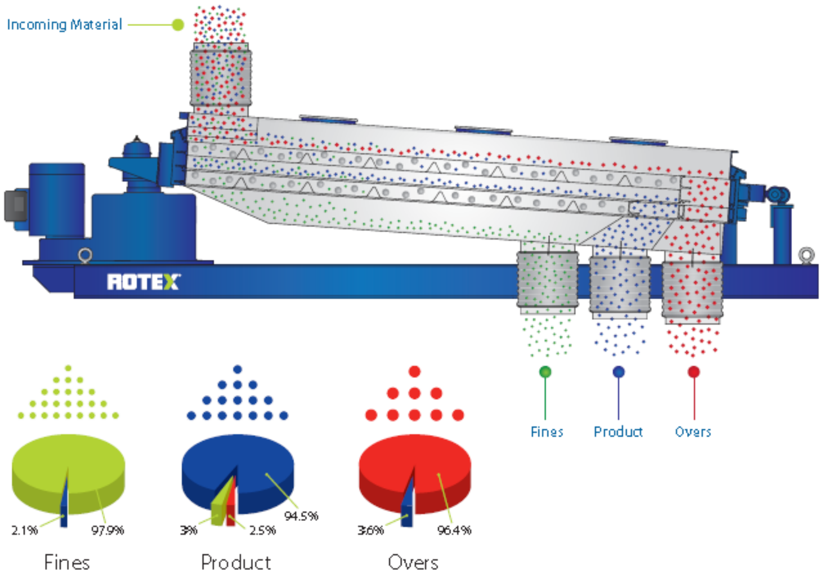
# Cyclones




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

# Screener

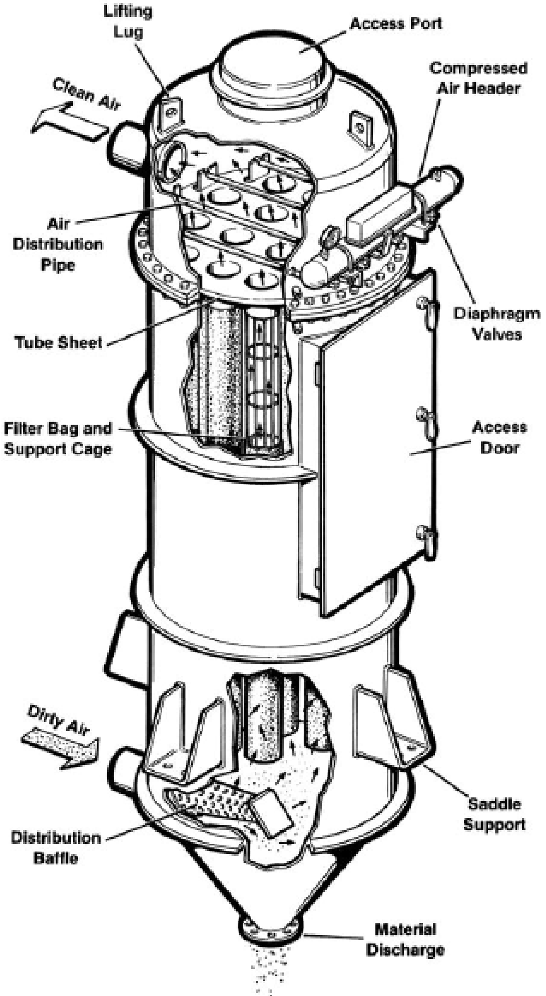




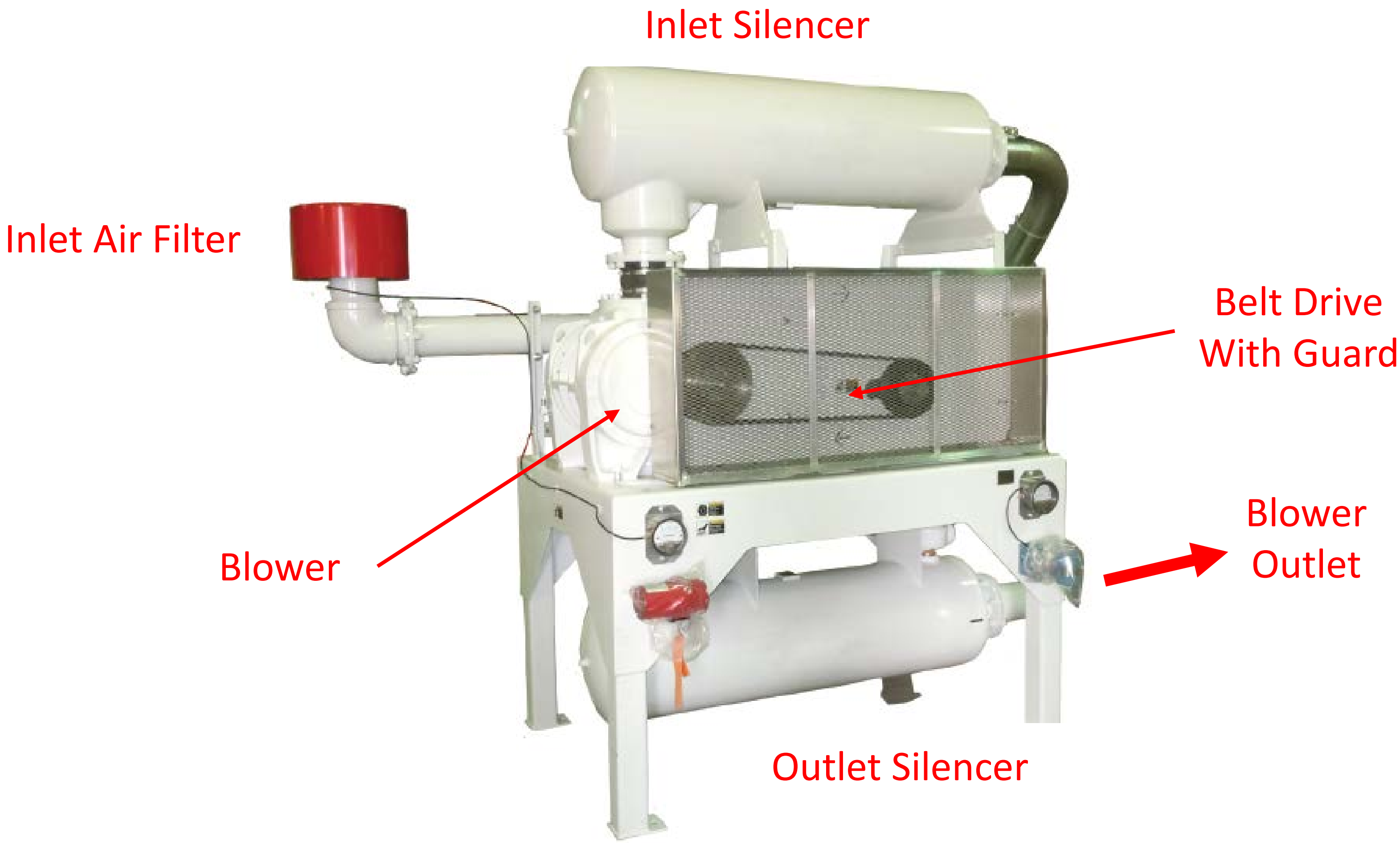

Rotex

# Filter Receiver

Flex-Kleen Model CT



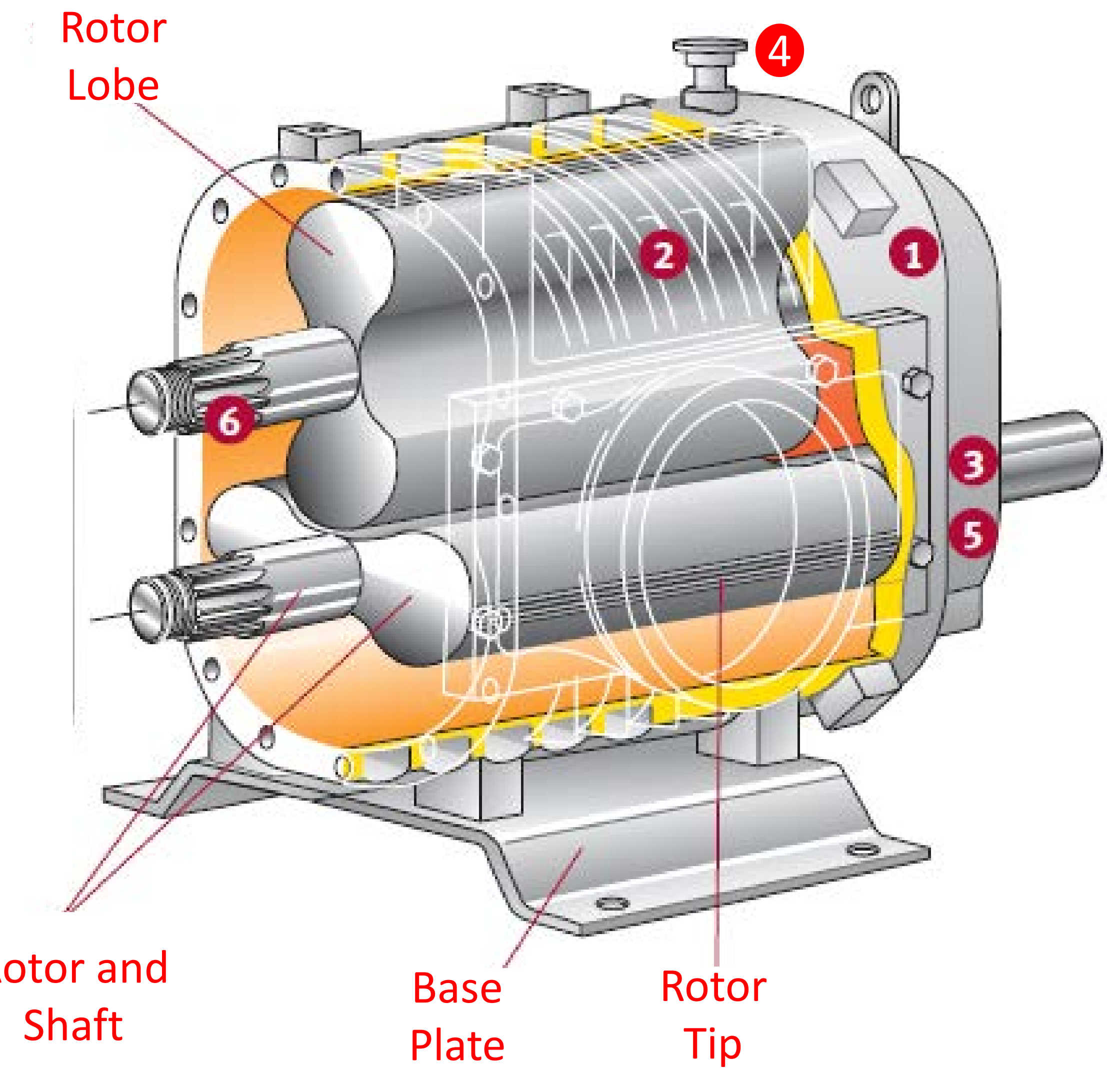
# Pressure Blower Package



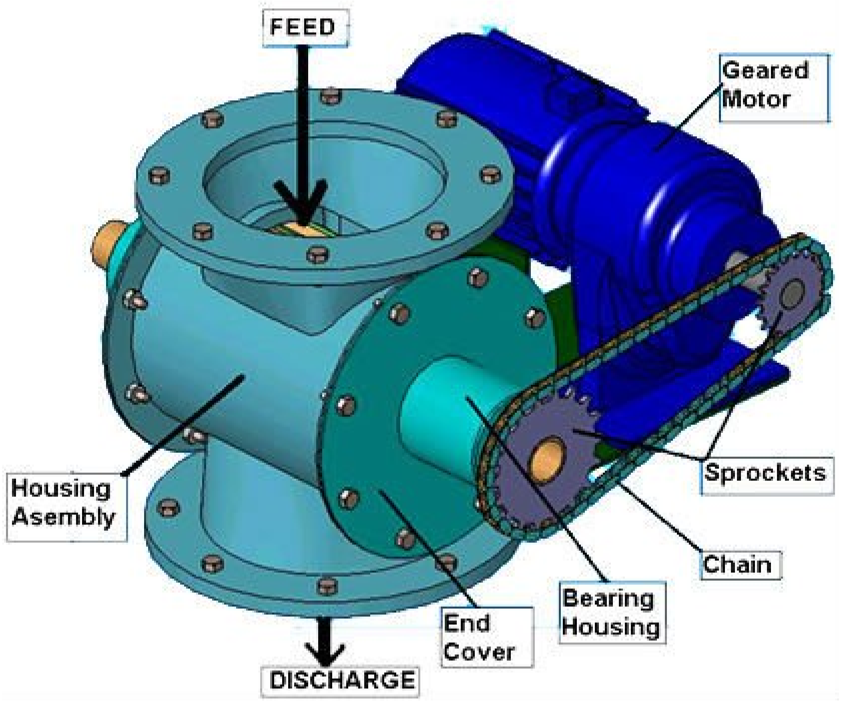
# Vacuum Blower Package

# Straight Rotary Lobe Blower

**1** - Case
**2** - Heat Dissipation Ribs
**3** – Bearing Housing
**4** - Oil Fill
**5** - End Plate
**6** – Shaft Splines For Timing Gears



# Rotary Valve



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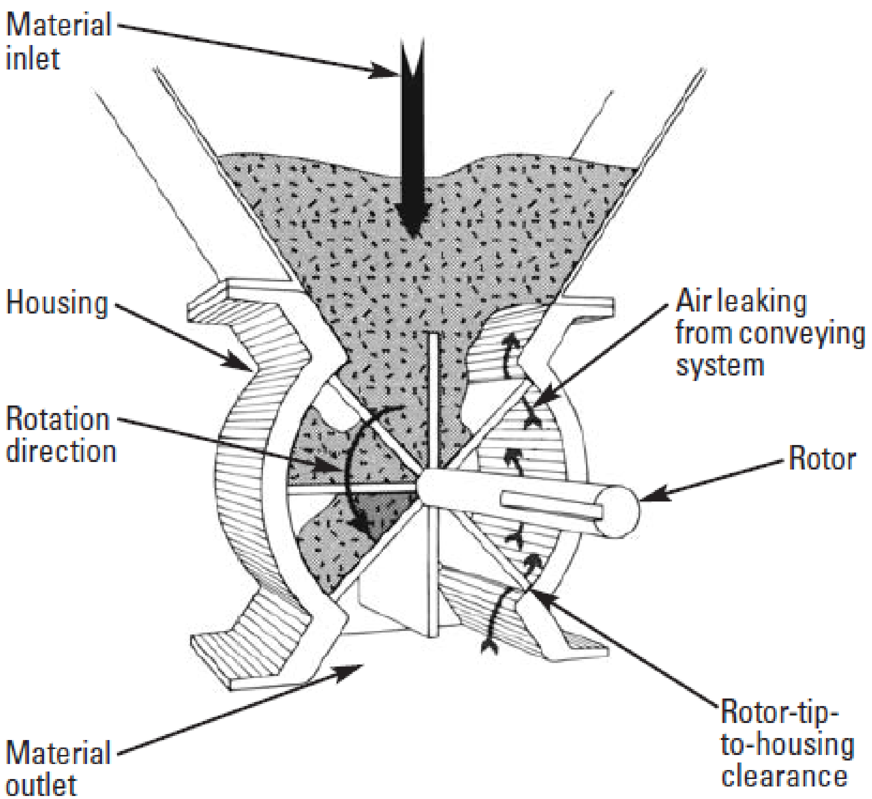
# Rotary Valve Venting

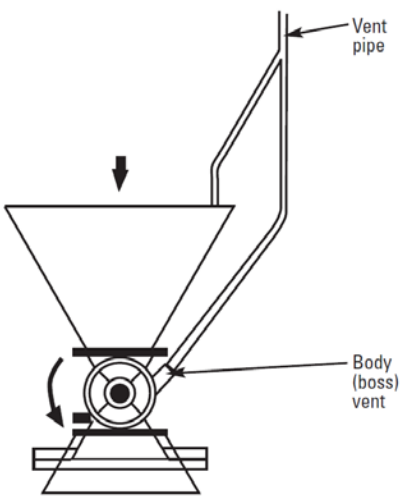
Air leaking through a rotary airlock valve




## Coperion K-TRON Aerolock

## Vented Shear Protector

Airlock body vent



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# Summary – PVC Design Drivers

- Reduce Batch Cycle Time
- Reduce Energy Cost Per Batch
- Minimize VCM Exposure Risk To Personnel