Delayed Coker Blowdown System
Water Reuse

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Delayed Coker Blowdown System Water Reuse

Topics:

(1) Blowdown System Overview
(2) Recycling BD Water
    => Constituents, Methods, Incentives & Risks
(3) Water System Layouts
(4) Coker Water Balance
(5) Adding Flash and/or Bleach Facilities

Special acknowledgement to Fritz Bernatz for his detailed evaluation and development of this technology
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General Overview of BD System Operations

(1) Receive Coke Bed Vapors during Stripping & Quenching

- Highest Normal Hydrocarbon Load => During Steam Stripping
- Highest Normal Steam Load => During Peak Quenching

(2) Receiving Coke Drum and/or Heater PRV Discharges

- Highest Abnormal Hydrocarbon Loads
  - => Majority of newer units receive the coke drum PRV
  - => Older units may receive furnace PRV because the Wilson-Snyder was not designed for pump shut-in pressure

(3) Receiving Wet (and Dry) Coke Drum Warm-Up Condensate / Gas

(4) Receive Start-Up and Shutdown Drain Slops

(5) Handle Foam Entrainment or a Coke Foamover
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General Overview of BD System Operations (cont’d)

Objectives

Cool Vapors on a Batch Basis

Separate feeds into five products

=> Heavy BD oil

=> Light BD oil

=> Non-condensable Gas

=> Sour Water

=> Coke

Be a Robust and Reliable Operation
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Modern Blowdown Design - 1

BD Condensers

PRV's

≤375°F

Heavy Drains

8 - 40 psig

300°F

Cooler

Demulsifier

Min Flow

Settler

NC

SWS

Seal Pot

Flare

Water

BD Gas

Lt Slop

Slop

≤375°F

≥375°F

Quench Vapors

Warm-Up Vapors

Make-up Gas Oil

Warm-Up Condensate

375°F

300°F

Steam Heater

Hot Contactor

Low Pres Lt Gases

2 - 10 psig

150°F

NC

NC

NC

Make-up Gas Oil

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Small Blowdown System & Water Tank

Hot Contactor

BD Condenser
Fin Fans

Cutting & Quench
Water Tank
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Blowdown Condenser Fin Fans

BD Condenser
Inlet
Distribution Piping

Fin Fan Bay
Isolation Valves
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DCU Blowdown Water Constituents*

H₂S, NH₃ and phenols will vary as the coke drum cycles from steam stripping to the end of coke bed quenching. Many factors will affect the concentrations:

- Resid type (S, N, geographical origin)
- Steam stripping operations (timing, duration, rates)
- Coke Bed size
- Blowdown System operations
  + Is water recycled for vapor desuperheating?
  + Size of BD Settler
  + Are downstream settling tanks used?

<table>
<thead>
<tr>
<th>BD Stage</th>
<th>H₂S</th>
<th>NH₃</th>
<th>Phenols</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam</td>
<td>100 - 200</td>
<td>40 - 120</td>
<td>15 - 60</td>
</tr>
<tr>
<td>Quench - start</td>
<td>100 - 400</td>
<td>100 - 175</td>
<td>15 - 60</td>
</tr>
<tr>
<td>Quench - mid</td>
<td>130 - 500</td>
<td>150 - 200</td>
<td>15 - 50</td>
</tr>
<tr>
<td>Quench - end</td>
<td>20 - 120</td>
<td>50 - 200</td>
<td>15 - 20</td>
</tr>
</tbody>
</table>

* Proper sampling protocols are needed to get accurate results
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Recycle of Condensed Blowdown Water

(1) Joliet Refinery has been recycling blowdown water since start-up in early 1970’s

=> Cited in Oil & Gas Journal 23-apr-1973
=> Heritage Mobil Oil technology
=> Blowdown water is flashed in closed-roof tank with vapor recovery
=> Coker water purge rate is high due to watery sludge addition and fines maze clean out with fire water, which reduces odors also due to dilution of constituents

(2) A refiner, no longer owned by ExxonMobil, has been recycling settled blowdown water to the cutting/quench water tank for over 30 years

=> Sodium Hypochlorite (Bleach) is added to cutting water in the fines settling lane
=> Coker water system purge rate was adjusted to balance sludge water addition
Incentives to Recycle Blowdown Water

Reduce Sour Water Stripper (SWS) Loadings

A typical SWS consumes around 1.3 lb of 150# steam / gal of feed, which allows the energy incentive to be calculated

\[
40,000 \text{ gal/drum} \times 1.5 \text{ drums/D/train} \times 365 \text{ D/yr} \\
\times 0.95 \text{ SF} \times 1.3 \text{ lb/gal} \times \$ Y/1000 \text{ lbs of steam}
\]

\[ \Rightarrow \$Z ZZ \text{ k/yr for each coke drum train} \]

conservatively assuming an 18 hr coking cycle

Reduced inorganic loading to the Waste Water Treatment Plant

Avoidance of capital expenditures for more SWS capacity

Reduced raw water make-up to the DCU

Elimination of mold in the quench/cutting water system and area
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Risks Considered with Recycling BD Water

- Exposure to low level H₂S and NH₃ emissions in the air
- Odors
- Increase in dissolved hydrocarbon levels in the recycled water
  
  => Function of BD System Water-HC Separation Efficiency

- Formation of chlorinated hydrocarbons
- Increased corrosion in cutting/quench water system

WWT Effects:
- Excess chlorine
- SO₄
- Chloramines
- AOX (Adsorbable Organic Halides)

All risks were evaluated and determined to be acceptable with proper facilities design and procedures
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Coker Water System - Sluiceway

[Diagram of the Coker Water System - Sluiceway]
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Coker Water System - Pit

Coke Drum

Overhead Gantry Crane

Conveyor to barge, rail or truck

Settling Labyrinth or Lane

Coke Pit

Cutting Water Tank

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Coker Water System - Pad

- Coke Drum
- Coke Pad
- Crushers
- Conveyor to barge, rail or truck
- Settling Labyrinth or Lane
- Cutting Water Tank

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**Water Balance**

Water Added to System:
- => Big Steam
- => Sludge Water
- => Pump Seal and Instrument Flushes
- => Water added for cleaning purposes
- => Rain

Water Leaving System:
- => Coke Moisture
- => Evaporation
- => Blowdown Water – Yes or No?
- => Addition or Purge?
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Water Balance – The Numbers

Basis:

=> 50 kB/D or 331 m3/hr or 8230 metric ton/D

=> 4-drum coker on 14 hour coking cycle; 28 hr drum cycle

<table>
<thead>
<tr>
<th>Water Added to System</th>
<th>Base Case BD to SWS</th>
<th>BD Water Recycled</th>
<th>Sludge Added</th>
<th>Sludge + Fines Lane Cleaning</th>
<th>Sludge + Fines Lane Cleaning</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kgal / Day</td>
<td>m3 /D</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>=&gt; Big Steam</td>
<td>13</td>
<td>49</td>
<td>49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>=&gt; Sludge</td>
<td>0</td>
<td>0</td>
<td>45</td>
<td>49</td>
<td>49</td>
</tr>
<tr>
<td>=&gt; Rain (annual avg)</td>
<td>2</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>=&gt; Pump Seal and Instrument Flushes</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>=&gt; Water added for cleaning purposes</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>20</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>58</td>
<td>228</td>
<td>304</td>
<td></td>
</tr>
</tbody>
</table>

Water Leaving System:

| => Coke Moisture      | 47                  | 178               | 178          | 178                         |                             |
| => Blowdown Water     | 132                 | 500               | 0            | 0                           | 0                           |
| => Evaporation        | 3                   | 11                | 11           | 11                          | 11                          |
|                       | 167                 | 631               | 39           | 115                         |                             |

Make-up / (Purge)

| Drain = 220 kgal / Day | 833 m3 /D |
| Cutting Water = 360 | 1363 m3 /D |
| Recycled Water from Pit/Pad = 580 kgal / Day | 2196 m3 /D |
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**Flashing the Blowdown Water**

- Minimum of 25% removal of H$_2$S and NH$_3$ at 0.14 barg (2 psig),

- Flashing at lower pressure is recommended to increase H$_2$S and NH$_3$ removal, but especially to remove hydrocarbons

  => Proper upstream blowdown operations are needed to properly separate oil and water

  => Steam Eductor on flash drum can create a very low pressure (0.01 barg)
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**Bleach Chemistry – H₂S**

*Sulfide Reactions*

At coker BD water pH range of 7.5 to 9.0 sulfides are typically in the form HS-

*Rapid Reactions*

**Bleach dissociation**

\[
NaOCl + H₂O \rightarrow HOCl + Na⁺ + OH⁻
\]

\[
HOCl \rightleftharpoons H⁺ + OCl⁻
\]

*(In equilibrium at 40-60% range based on pH)*

*Reaction of Bleach with sulfides at low excess chlorine (under acidic conditions)*

\[
H₂S + HOCl \rightarrow H⁺ + S⁰ + Cl⁻ + H₂O
\]

*Reaction of Bleach with sulfides (under alkaline conditions)*

\[
H₂S + 4 NaOCl > H₂SO₄ + 4 NaCl
\]
Ammonia Reactions

Chlorine/Ammonia reactions at a ratio of less than equimolar will not form free chlorine. Blowdown water treatment will be in dilute aqueous solutions.

\[
\text{HOCl} + \text{NH}_3 \rightarrow \text{NH}_2\text{Cl} \quad \text{(monochloroamine)} \quad + \text{H}_2\text{O}
\]

- Ratio of chlorine to ammonia is equimolar (5:1 by wt) or less
- Monochloroamine preferred at pH >7.5

Organic compounds

\[
\text{R} + \text{HOCl} \rightarrow \text{RCl} + \text{H}_2\text{O}
\]

- Expected organic compounds are slow to react.
- Any excess bleach will react with ammonia

Monochloroamines are slow to react with organic matter
AOX Considerations for the Waste Water Treating Plant

- Adsorbable Organic Halides (AOX) is a measure of the organic halogen load... These organic halides are released in wastewater from the oil, chemical, and paper industries.
- Chloro-organics are a type of AOX
- Chloro-organics *may* be formed by bleach addition to the Blowdown reuse water and may be sent to the WWTP through the water purge.
- This should be considered relative to WWTP permits.
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Example Bleach Operations for a Hypothetical DCU

Basis

=> 50 kBD (331 m3/h) fresh feed

=> Sulfur = 4.5 wt%;  Nitrogen =  0.8 wt%

Design Basis needs to determine how much of the worst case sulfides and ammonia need to be treated. One option is:

=> Sulfide treatment at stoichiometric level

=> Ammonia treatment at 50% stoichiometric level

Other factors to consider:

=> Benchmarking with other water-chemical dosing programs

=> Can you take credit taken for pre-flash of water?

Facility design should have % overdesign factor