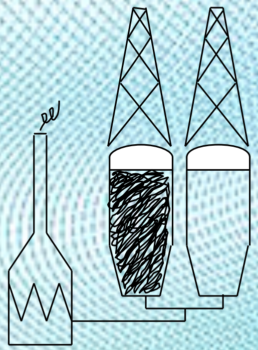
ExxonMobil

Delayed Coker Blowdown System Water Reuse

REFCOMM BUDAPEST 2017



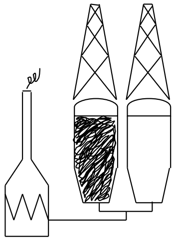
Energy lives here™

Presented by Mitch Moloney of **ExxonMobil Research & Engineering**

mitchell.j.moloney@exxonmobil.com

Budapest Hungary   coking.com   October-2017

Delayed Coker Blowdown System Water Reuse



Topics:

(1) Blowdown System Overview

(2) Recycling BD Water

=> Constituents, Methods, Incentives & Risks

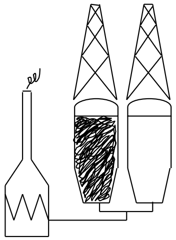
(3) Water System Layouts

(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

Delayed Coker Blowdown System Water Reuse



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

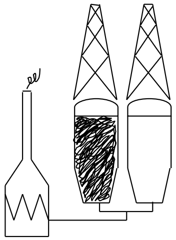
=> Older units may receive furnace PRV because the Wilson-Snyder was not designed for pump shut-in pressure

(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

Delayed Coker Blowdown System Water Reuse



General Overview of BD System Operations (cont'd)

Objectives

Cool Vapors on a Batch Basis

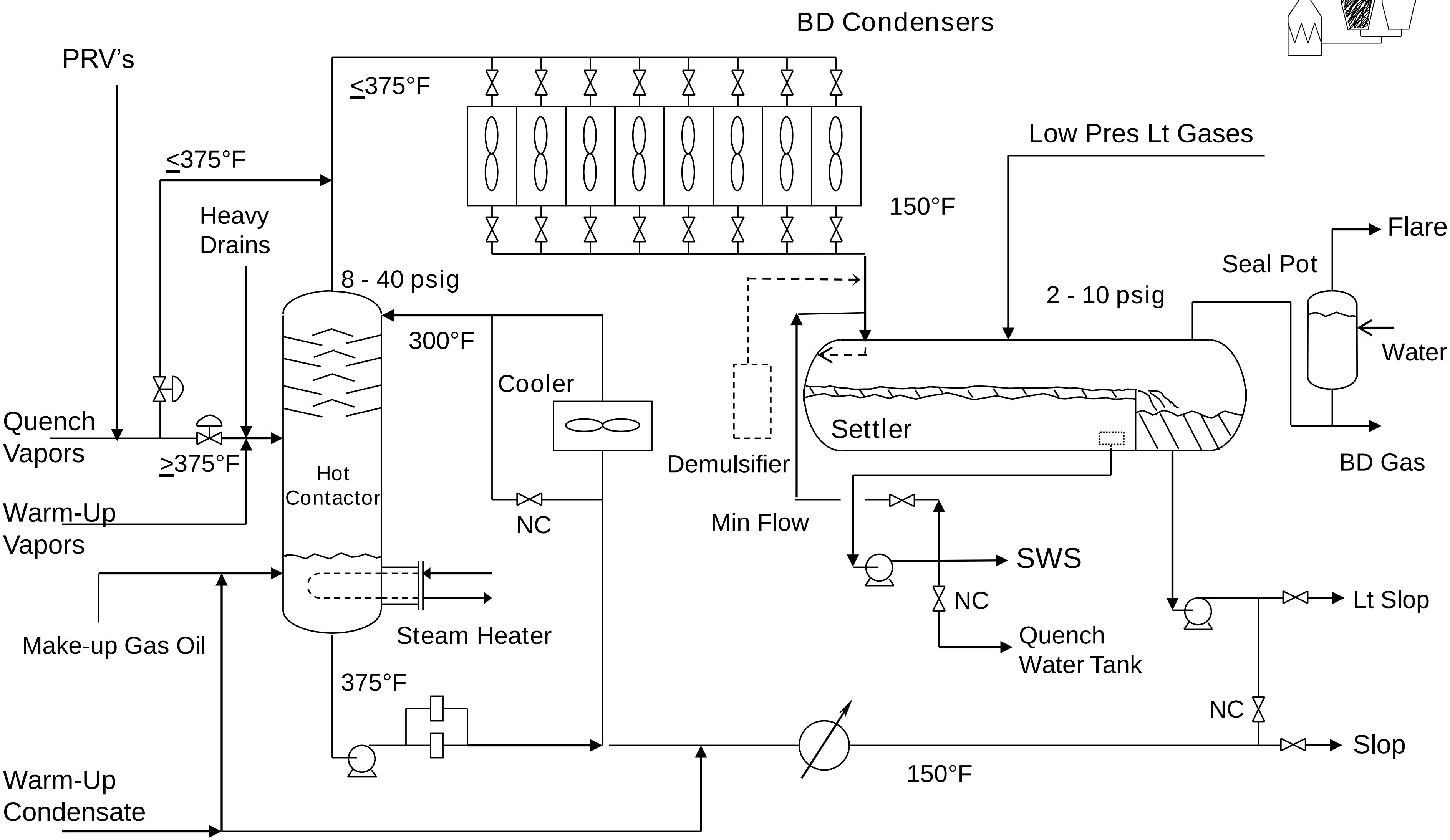
Separate feeds into five products

- => Heavy BD oil
- => Light BD oil
- => Non-condensable Gas
- => Sour Water
- => Coke

Be a Robust and Reliable Operation

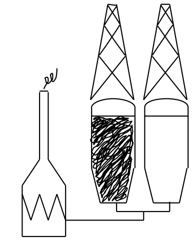
Delayed Coker Blowdown System Water Reuse

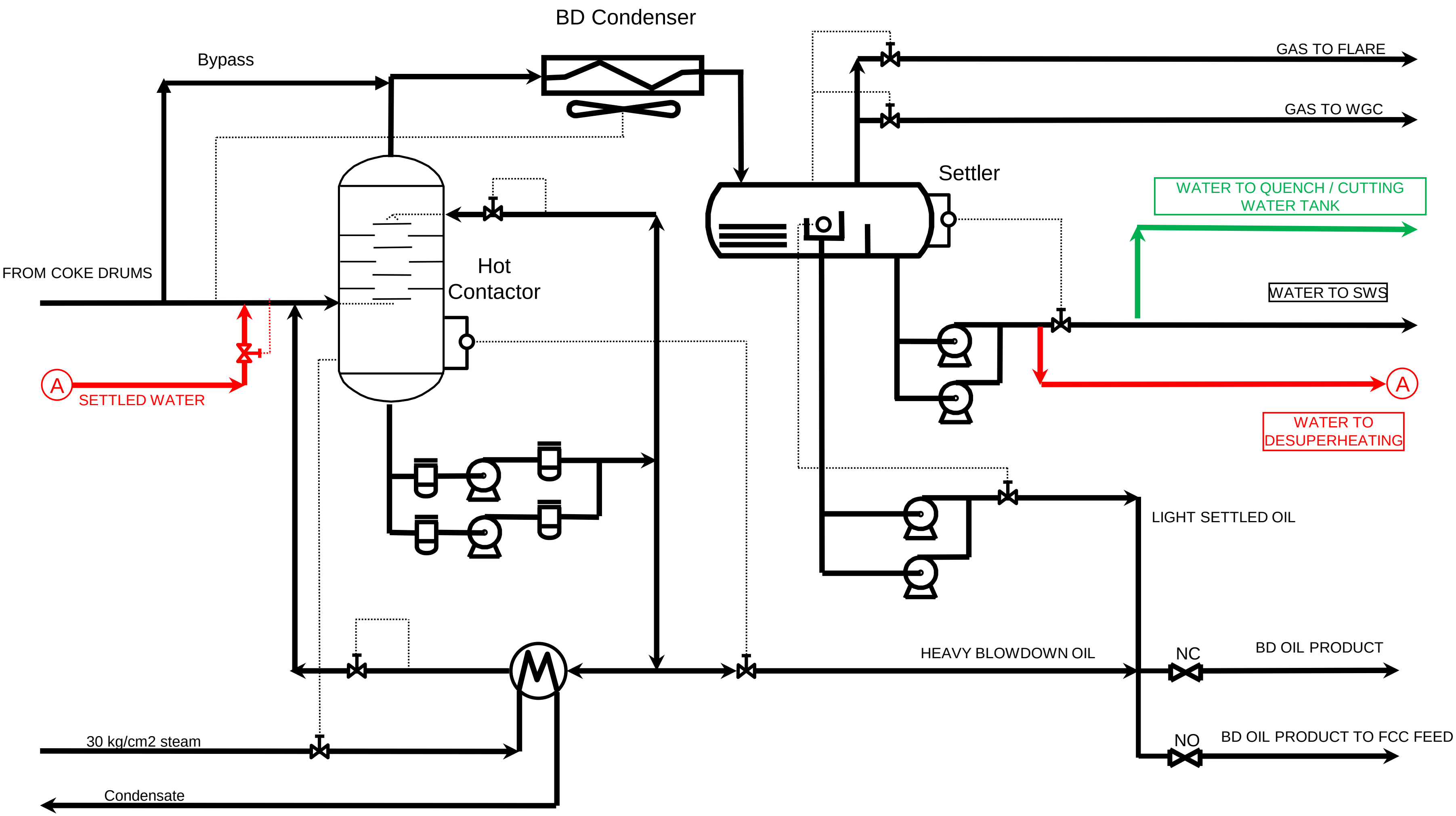
Modern Blowdown Design - 1



Delayed Coker Blowdown System Water Reuse

Modern Blowdown Design - 2





Delayed Coker Blowdown System Water Reuse

Small Blowdown System & Water Tank

Hot Contactor

BD Condenser
Fin Fans

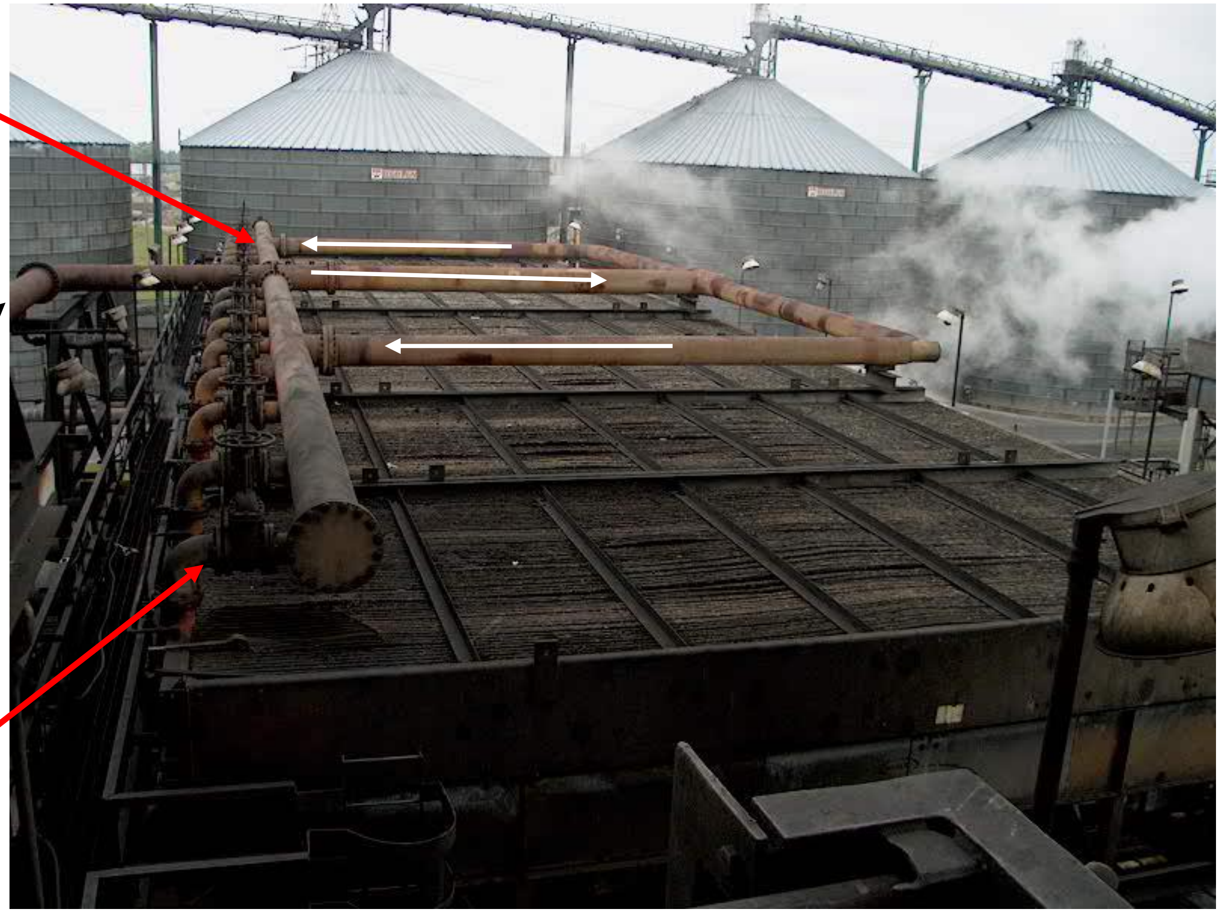
Cutting & Quench
Water Tank

Delayed Coker Blowdown System Water Reuse

Blowdown Condenser Fin Fans

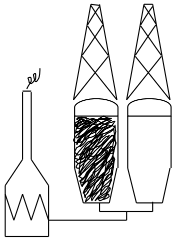
BD Condenser Inlet Distribution Piping

INLET



Fin Fan Bay Isolation Valves

Delayed Coker Blowdown System Water Reuse



DCU Blowdown Water Constituents*

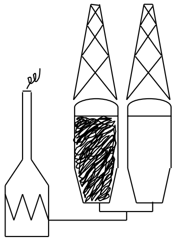
H_2S, NH_3 and phenols will vary as the coke drum cycles from steam stripping to the end of coke bed quenching. Many factors will affect the concentrations:

- 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?

BD Stage	H_2S	NH_3	Phenols
Steam	100 - 200	40 - 120	15 - 60
Quench - start	100 - 400	100 - 175	15 - 60
Quench - mid	130 - 500	150 - 200	15 - 50
Quench - end	20 - 120	50 - 200	15 - 20

* Proper sampling protocols are needed to get accurate results

Delayed Coker Blowdown System Water Reuse



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

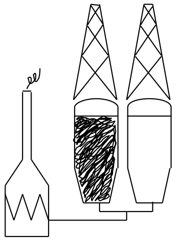
=> Coker water purge rate is high due to watery sludge addition and fines maze clean out with fire water, which reduces odors also due to dilution of constituents

(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

Delayed Coker Blowdown System Water Reuse



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 gal /drum * 1.5 drums/D/train * 365 D/yr
* 0.95 SF * 1.3 lb/gal * $ Y/1000 lbs of steam

=> $ZZZ k / yr for each coke drum train
conservatively assuming an 18 hr coking cycle

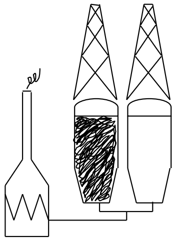
Reduced inorganic loading to the Waste Water Treatment Plant

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

Delayed Coker Blowdown System Water Reuse



Risks Considered with Recycling BD Water

Exposure to low level H_2S and NH_3 emissions in the air

Odors

Increase in dissolved hydrocarbon levels in the recycled water
=> Function of BD System Water-HC Separation Efficiency

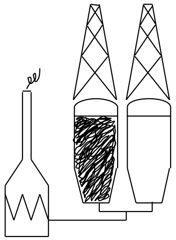
Formation of chlorinated hydrocarbons

Increased corrosion in cutting/quench water system

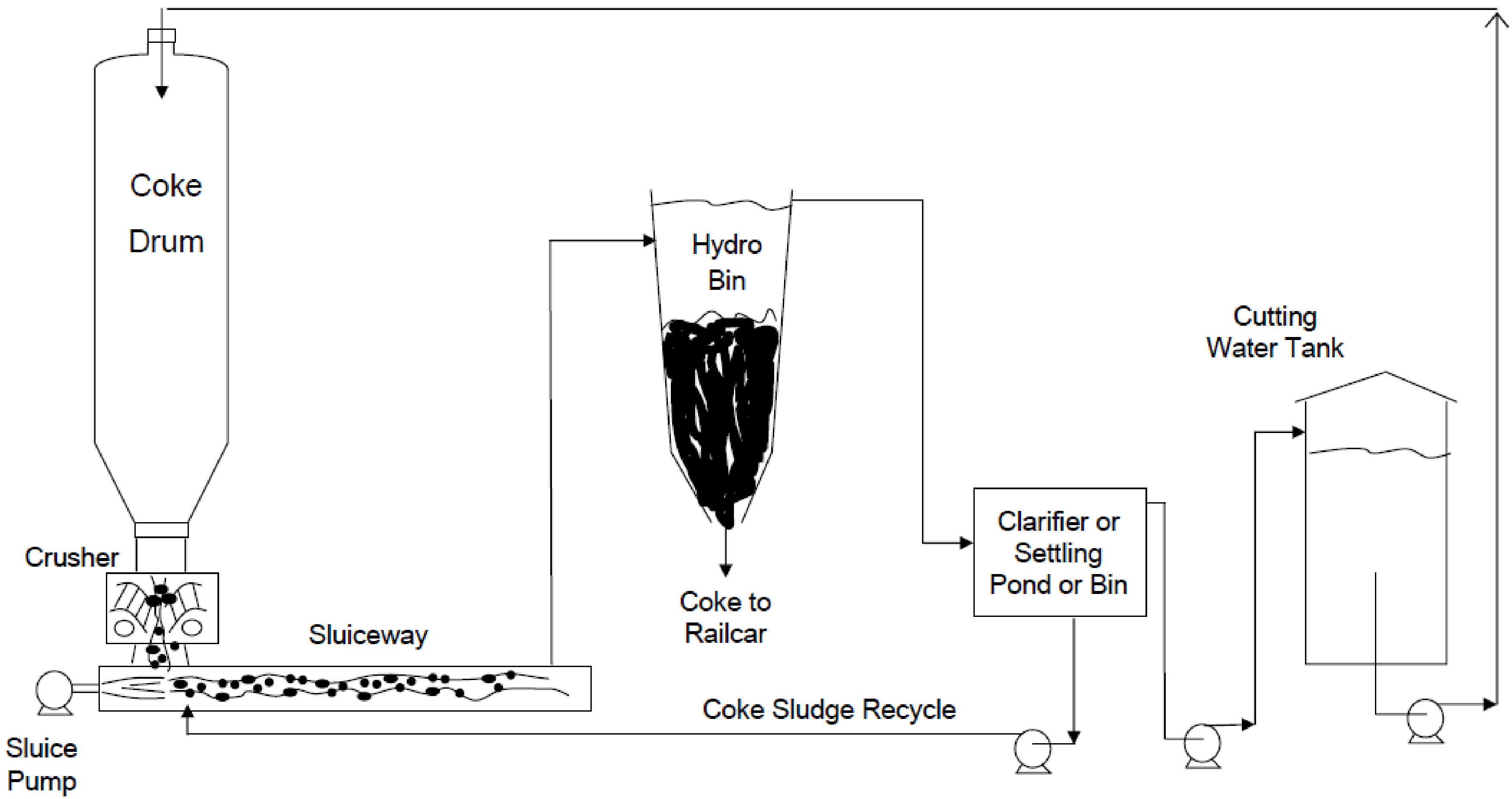
WWT Effects:
- Excess chlorine
- SO_4
- Chloramines
- AOX (Adsorbable Organic Halides)

All risks were evaluated and determined to be acceptable with proper facilities design and procedures

Delayed Coker Blowdown System Water Reuse

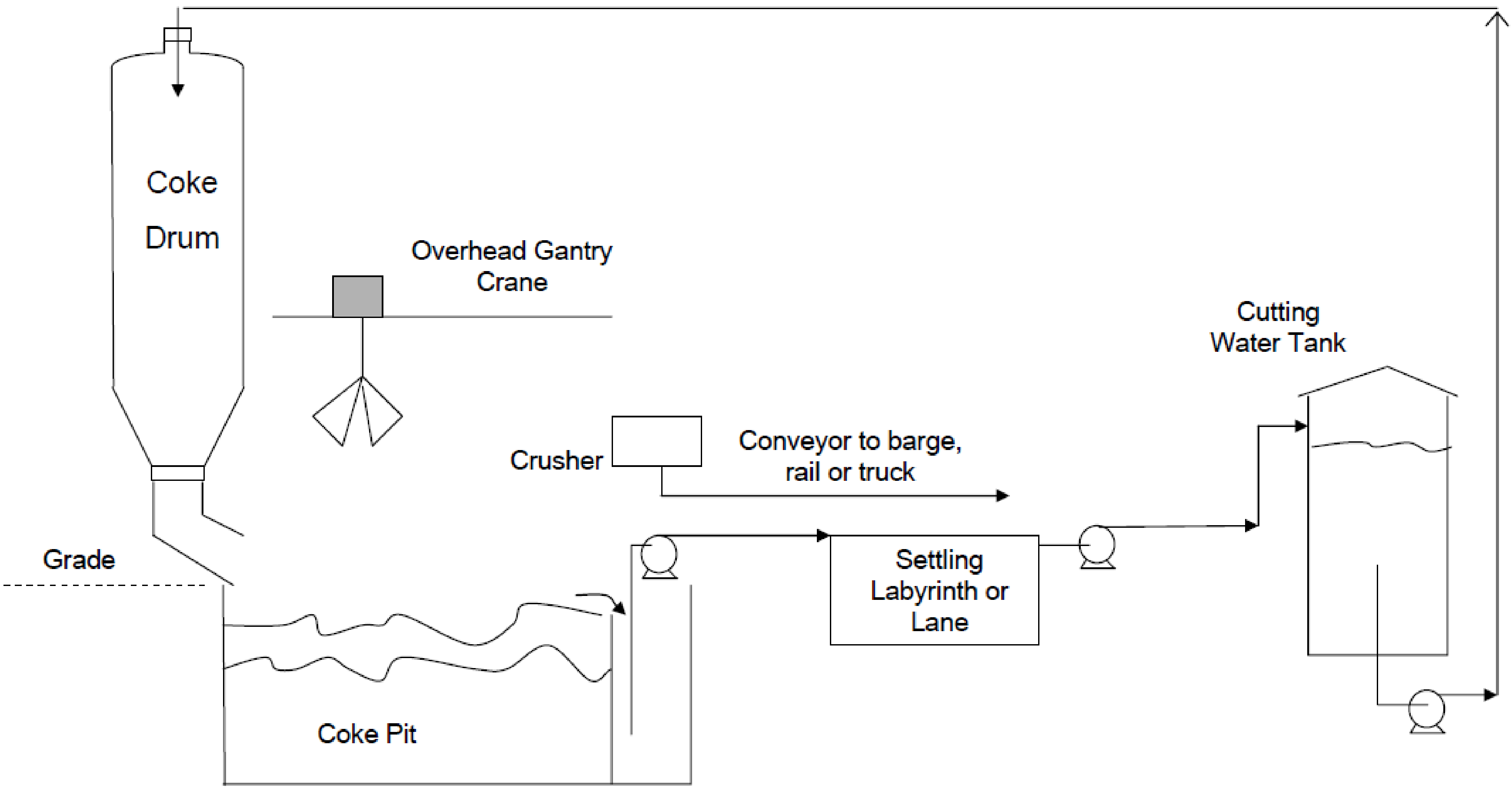


Coker Water System - Sluiceway



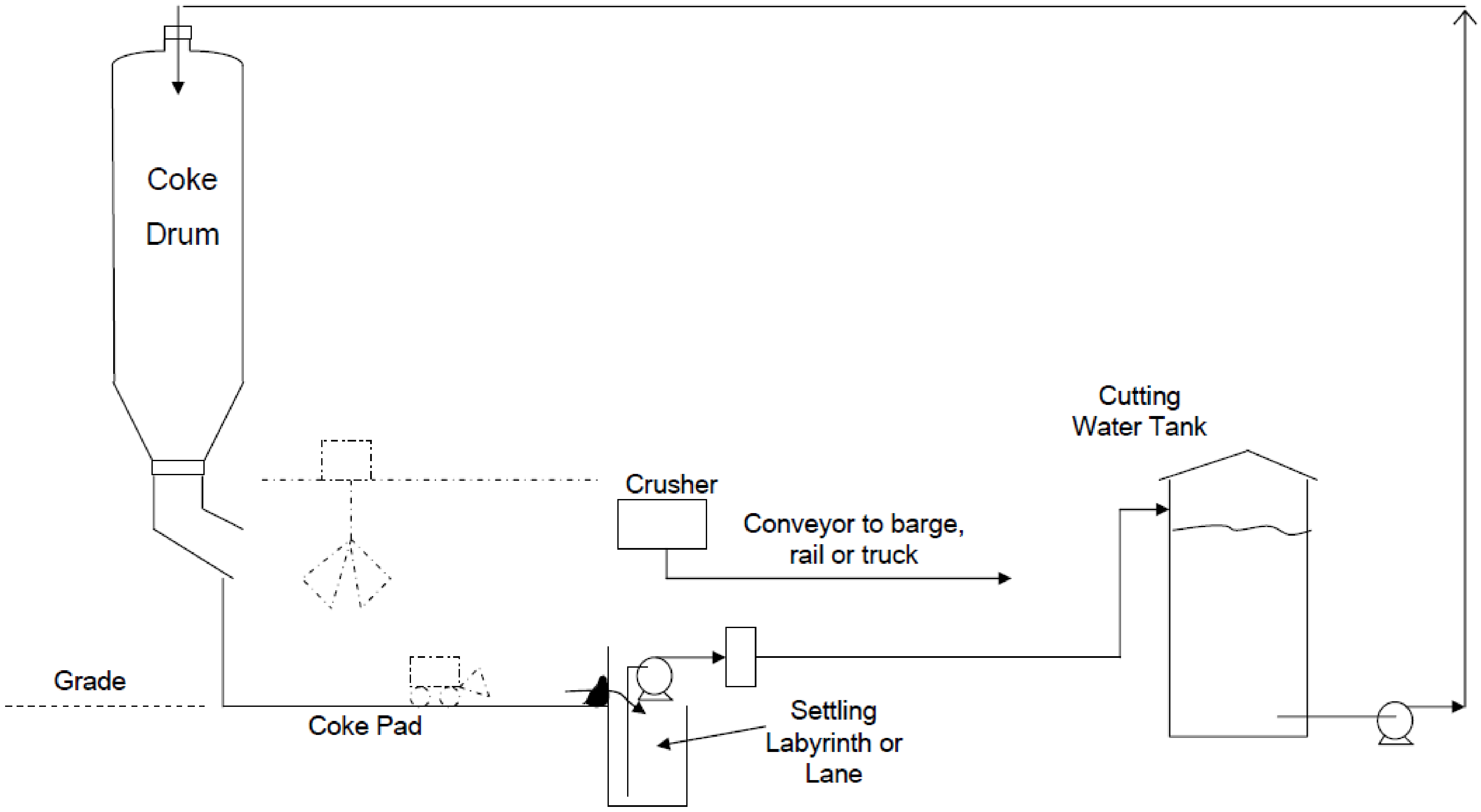
Delayed Coker Blowdown System Water Reuse

Coker Water System - Pit

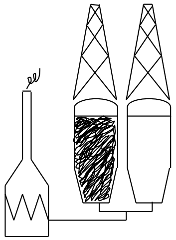


Delayed Coker Blowdown System Water Reuse

Coker Water System - Pad



Delayed Coker Blowdown System Water Reuse



Water Balance

Water Added to System:

=> Big Steam

=> Sludge Water

=> Pump Seal and Instrument Flushes

=> Water added for cleaning purposes

=> Rain

Water Leaving System:

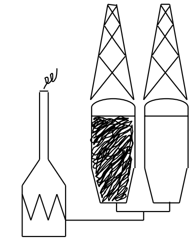
=> Coke Moisture

=> Evaporation

=> Blowdown Water – Yes or No?

=> Addition or Purge?

Delayed Coker Blowdown System Water Reuse



Water Balance – The Numbers

Basis:

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

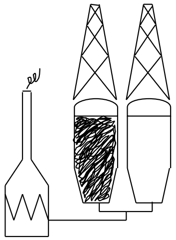
=> 4-drum coker on 14 hour coking cycle; 28 hr drum cycle

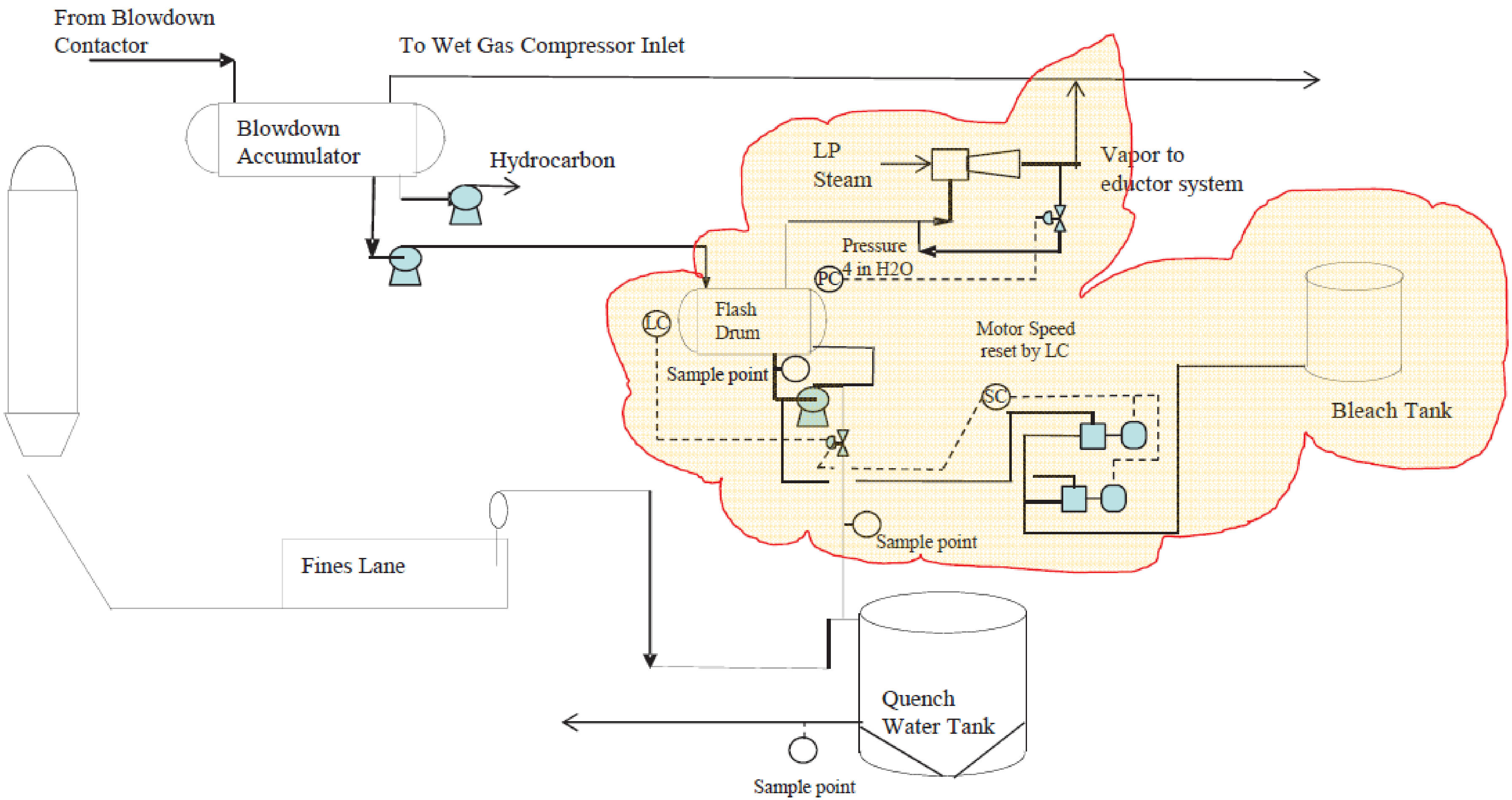
	Base Case BD to SWS	BD Water Recycled	Sludge Added	Sludge + Fines Lane Cleaning	Base	BD Water Recycled	Sludge Added	Sludge + Fines Lane Cleaning
	kgal / Day				**m^3/D**			
Water Added to System								
=> Big Steam	13	13	13	13	49	49	49	49
=> Sludge	0	0	45	45	0	0	170	170
=> Rain (annual avg)	2	2	2	2	6	6	6	6
=> Pump Seal and Instrument Flushes	1	1	1	1	3	3	3	3
=> Water added for cleaning purposes	0	0	0	20	0	0	0	76
	15	15	60	80	58	58	228	304
Water Leaving System:								
=> Coke Moisture	47	47	47	47	178	178	178	178
=> Blowdown Water	132	0	0	0	500	0	0	0
=> Evaporation	3	3	3	3	11	11	11	11
Make-up / (Purge)	167	35	(10)	(30)	631	131	(39)	(115)

Drain =	220		833	
Cutting Water =	360		1363	
Recycled Water from Pit/Pad =	580	kgal/D	2196	m3/D

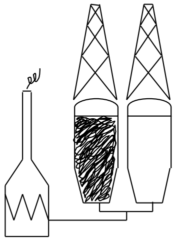
Delayed Coker Blowdown System Water Reuse

Coker Water System - Pad





Delayed Coker Blowdown System Water Reuse



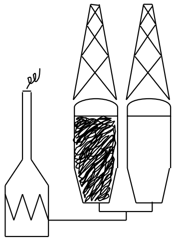
Flashing the Blowdown Water

- Minimum of 25% removal of H_2S and NH_3 at 0.14 barg (2 psig),
- Flashing at lower pressure is recommended to increase H_2S 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)

Delayed Coker Blowdown System Water Reuse



Bleach Chemistry – H_2S

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

$$NaOCl + H_2O \rightarrow HOCl + Na^+ + OH^-$$

$$HOCl \Leftrightarrow H^+ + OCl^-$$

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

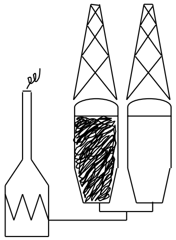
Reaction of Bleach with sulfides at low excess chlorine (under acidic conditions)

$$H_2S + HOCl \rightarrow H^+ + S^0 + Cl^- \; H_2O$$

Reaction of Bleach with sulfides (under alkaline conditions)

$$H_2S + 4\ NaOCl > H_2SO_4 + 4\ NaCl$$

Delayed Coker Blowdown System Water Reuse



Bleach Chemistry – NH_3

Ammonia Reactions

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

$HOCl + NH_3 \rightarrow NH_2Cl$ *(monochloroamine)* $+ H_2O$

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

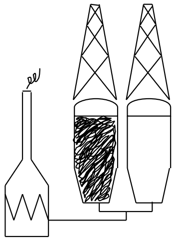
Organic compounds

$R + HOCl \rightarrow RCl + H_2O$

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

Monochloroamines are slow to react with organic matter

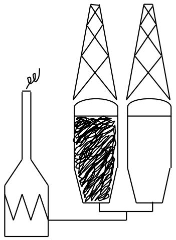
Delayed Coker Blowdown System Water Reuse



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.

Delayed Coker Blowdown System Water Reuse



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