Wet Scrubbing Control Technology

For FCCU’s

Particulate, SO₂, SO₃ and NOₓ

Removal

In One Process Unit

Garrett Billemeeyer - Belco Technologies Corp.
BELCO® - Providing Proven Technologies

- EDV® Wet Scrubbing Systems

- Linde/BOC’s LoTOx NOx Reduction Process

(LoTOx™ is a trademark of The BOC Group)
BELCO®’s List of Scrubbing Experience In Refineries

- **North America (41)**
  - Valero (9)
  - Coastal
  - Marathon/Ashland (2)
  - Quakerstate (Pennzoil)
  - Irving Oil
  - Motiva
  - ConocoPhillips (5)
  - Premcor (4) (now Valero)
  - Shell Oil
  - Lion Oil
  - Citgo (3)
  - Sunoco (4)
  - BP
  - Placid
  - Western
  - Petrobras
  - HollyFrontier (3)
  - Tesoro

- **India (9)**
  - IOCL (4)
  - ESSAR
  - HPCL (3)
  - NOCL

- **Other (48)**
  - Taiwan - Formosa (5), Chinese Petroleum
  - Korea – SK, GS Caltec, Hyundai
  - Qatar – NODCO, Al Shaheen
  - Italy – Eni S.p.A.
  - Norway – ESSO
  - Switzerland – Tamoil
  - Saudi Arabia - SAMREF
  - Russia – GAZPROM
  - Philippines – Petron (2)
  - Belgium – Total
  - Thailand – Star Petroleum
  - Brazil – Petrobras REFAP
  - China – Petrochina (13), Sinopec (11), Western Pacific, Sinochem (3)
  - UAE – Takreer
  - Canada – PetroBank
  - Romania – Petrotel/Lukoil

106 EDV Wet Scrubbing Systems in Refineries
(94) are on FCCU applications)
Why EDV® Wet Scrubbing for FCCU?

- High Collection Efficiency for Particulate, SO\textsubscript{X} and now NO\textsubscript{X} all in one step
- Proven Design Features for >5+ Year “Non-Stop” Operation
- Proven Capability to Handle FCC Upsets/Reversals
  - Very High Particulate Carry Over
  - High Temperature Excursions (& COB Bypass)
- Proven Capability to Handle Very Abrasive Particulate
- Proven Capability to Allow Large Gas Flow Variations
- Proven Flexibility to Allow Expansion and Feed Changes
- Ability to be designed as a Regenerative Scrubbing System when using LABSORB™
- Perfectly suited for NOx removal LoTOx™ application
EDV® Wet Scrubbing
(Typical Upflow Configuration)

- Stack
- Filtering Modules
- Quench Section
- Droplet Separators (built inside scrubber)
- Absorber Section
- Nozzles form Spray Curtains
EDV® Wet Scrubbing
Quench & Spray Tower

Quench Section

Absorber/Spray Tower Section
EDV® Wet Scrubbing
Spray Tower

- Coarse PM, SO$_2$ & SO$_3$ (plus NO$_x$ when LoTOx™ is applied)
  - High Liquid / Gas Contact
    Cross Sectional Dense Water/Caustic Curtains
    SO$_2$ & NO$_x$ Absorption/PM & SO$_3$ Impaction
  - Staged Approach for More Reliable scrubbing
- Open Tower
- Continuously Washed Walls for Self Cleaning
- No Mist Formation
- Low Pressure Drop (No Pressure Drop Design is also Available)
EDV® Wet Scrubbing

G® Nozzle

X -Section
EDV® Wet Scrubbing
(G®-400 Nozzle) Cross Section

Creates a Dual Reagent Spray by means of a Declining Trough Design
Single G® Nozzle Operation
EDV® Wet Scrubbing
Filtering Modules
EDV® Filtering Module
Condensation & Filtration

- Fine PM & SO$_3$ Mist Collection
  - By Acceleration, Adiabatic Expansion and Super Saturation
  - Condensation
  - Particle Size Growth
  - Filtration
- Open / Self Cleaning
- Non-plugging Design
- No Mist Formation
- Low Pressure Drop
EDV® 5000 Filtering Module
Efficient Fine Particulate Control

Condensation & Agglomeration of Fine Particulate & Sulfuric Acid Mist

Cleaned Gas on to Droplet Separation

CLEANED GAS ON TO DROPLET SEPARATION

Liquid to Spray

Gas Inlet

Fine Particulate Encased in large water droplet

Fine Particulate
EDV® 5000 Filtering Module
F-130 Spray Nozzle

Filtering Module
F130 Spray Nozzle
EDV® Wet Scrubbing
Particulate Control/Size Distribution

% LESS THAN

PARTICLE SIZE (MICRONS)

Unit A
Unit B
Unit C
Unit D
Unit E
EDV® Wet Scrubbing
Particulate Control/Absorber G-Nozzle Collection

COLLECTED BY G-NOZZLE

PARTICLE SIZE (MICRONS)

% LESS THAN

UNITS

- Unit A
- Unit B
- Unit C
- Unit D
- Unit E

DUPONT BELCO
The balance of the particles smaller than 3 micron are then grown by condensation and scrubbed the EDV® Filtering Module.
EDV® 6000 Filtering Module
Very Efficient Fine Particulate Control

Cleaned Gas on to Droplet Separation

Liquid to Spray

Condensation & Agglomeration of Fine Particulate & Sulfuric Acid Mist

Cleaned Gas on to Droplet Separation

Fine Particulate Encased in large water droplet

Gas Inlet

Liquid to Spray
Removal of Excess Water Droplets without mist eliminators
EDV® Wet Scrubbing
Droplet Separators
EDV® Droplet Separator

- Removes Droplets Carryover From Gas Stream
- Low Pressure Drop
- Non-Plugging Design
- Open /Self Cleaning
- No Mists Eliminators
- No Moving Parts
CYCLOLAB Droplet Separator
EDV® Wet Scrubbing System
Droplet Separators
CYCLOLAB Droplet Separator
EDV® Scrubbing System
Two Simple Process Flows

EDV® ABSORBER
DIRTY FLUE GAS FROM FCC
EDV® QUENCH
OVERFLOW DRAINS
EDV® DROPLET SEPARATORS
EDV® FILTERING MODULES (for EDV 5000 & 6000 models only)
MAKEUP WATER
CLEAN GAS OUT
GAS OUT

EDV® STACK

(This loop is for EDV® 5000, and 6000 models only)
(for EDV® 5000 and 6000 models only)
SLIPSTREAM TO PURGE TREATMENT UNIT

pHC
pHC
pHC

SLIPSTREAM TO PURGE TREATMENT UNIT

MAKEUP WATER

SLIPSTREAM TO PURGE TREATMENT UNIT

SLIPSTREAM TO PURGE TREATMENT UNIT

SLIPSTREAM TO PURGE TREATMENT UNIT
Daily Monitoring (minimal)

a) General Walk-down of Entire System

b) Monitor pH and SO$_2$ levels

c) Monitor pressure readings for the Tower Recycle Pumps and Quench nozzles.

d) Monitor Delta ‘P’ for the Filtering Module Loop.

e) Monitor Clarifier Sludge Build-up
Treatment of Scrubber Purge
EDV® Wet Scrubbing

Purge Treatment Unit
EDV® Wet Scrubbing
Typ. Purge Treatment Unit - PFD with Settling Bin

- SCRUBBER
  - PURGE
  - FLOCCULENT
  - OVERFLOW TANK
  - OVERFLOW PUMP

- CLARIFIER
  - UNDERFLOW PUMP
  - FILTER
  - PRESS

- OXIDATION TOWERS
  - CAUSTIC ADDITION
  - EFFLUENT DISCHARGE

- SETTLING BINS
  - 50% Solids Non Hazardous

- AIR BLOWER

50% Solids Non Hazardous
EDV® Wet Scrubbing System

Purge Treatment Unit -- Effluent

- Discharge of Scrubber Water
  - Reduction of Suspended Solids (TSS) down to below 200 ppm
  - Reduction of Chemical Oxygen Demand from Sulfites (COD) down to below 100 ppm
- More Stringent Effluent Specifications can be met if required
PTU for 60,000 bpsd FCCU

Clarifier

Oxidation Towers

Settling Bins
EDV® Wet Scrubbing
Purge Treatment Unit - Settling Bins

Clarifier Underflow Dumping to Settling Bin

Dried Catalyst Fines
EDV® Wet Scrubbing

Easily Modified for NO$_x$ Control with LoTOx™

- Low Temperature Oxidation
  -

LoTOx™ is a trademark of the BOC Group
LoTO$_x^{TM}$ Installation on an FCCU
EDV® Wet Scrubber with LoTO$_x^{TM}$

- SO$_2$ & Particulate Removal
- No x Removal
- Water Droplet Separation
- Fine Particulate Removal
EDV® Wet Scrubbing System
With LoTOx™ injection

Ozone Injection after Quench

Conversion to $\text{N}_2\text{O}_5$

Conversion to Nitric Acid

Conversion to Sodium Nitrate by contact with scrubber reagent

Nitrates removed with Scrubber Purge

$\text{N}_2\text{O}_5$ Conversion to $\text{HNO}_3$ and Scrubbing by EDV Nozzles

NO, NO$_x$ Conversion to $\text{N}_2\text{O}_5$
EDV® Wet Scrubbing System
With LoTOx™ injection

*Simplified LoTOx™ Chemistry*

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]

\[ 2\text{NO}_2 + \text{O}_3 \rightarrow \text{N}_2\text{O}_5 + \text{O}_2 \]

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 \]

\[ \text{HNO}_3 + \text{NaOH} \rightarrow \text{NaNO}_3 + \text{H}_2\text{O} \]
Rate of Reaction

Low Temperature Oxidation of NOx:

Rate (k) = cm³/molecule/sec
(298 degrees K)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO + O₃ ----&gt; NO₂ + O₂</td>
<td>k = 1.8 x 10⁻¹⁴</td>
</tr>
<tr>
<td>2 NO₂ + O₃ ----&gt; N₂O₅ + O₂</td>
<td>k = 3.5 x 10⁻¹⁷</td>
</tr>
<tr>
<td>CO + O₃ ----&gt; CO₂ + O₂</td>
<td>k &lt; 1.1 x 10⁻²¹</td>
</tr>
<tr>
<td>SO₂ + O₃ ----&gt; SO₃ + O₂</td>
<td>k = 2.2 x 10⁻²²</td>
</tr>
</tbody>
</table>

Ozone is highly selective for NOx due to the rapid reaction rate. NOx is rapidly converted to water soluble species:

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 \]  
(Liquid Phase)
### EDV® Wet Scrubbing System

**With LoTOx™ injection**

<table>
<thead>
<tr>
<th>Species</th>
<th>Relative Solubility at 25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>1</td>
</tr>
<tr>
<td>NO₂</td>
<td>20</td>
</tr>
<tr>
<td>SO₂</td>
<td>2000</td>
</tr>
<tr>
<td>N₂O₅</td>
<td>&gt;&gt; 2000</td>
</tr>
<tr>
<td>HNO₃</td>
<td>Mixes with water in all proportions</td>
</tr>
</tbody>
</table>
LoTOx™ Process
Ozone Generation

1. Feedgas
   - LOX Tank or pipeline
   - $O_2$

2. Energy
   - (480 V/60Hz)

- Power supply unit
- Chiller
- Ozone generator (grounded)

- OZONE
LoTOx™ Process
Ozone Generation
LoTOx™ Process
Ozone Generation

1370 Lbs/day OZONE GENERATOR - OZONE SIDE OPEN
LoTOx™ Process
Ozone Generation

Single Ozone Generator Cell Dielectric

\[ 3O_2 \rightleftharpoons 2O_3 \]
EDV® Wet Scrubbing System
Ozone Injection
DIRTY FLUE GAS FROM FCC
EDV® ABSORBER W/RESIDENCE TIME
EDV QUENCH
Ozone Injection
EDV® FILTERING MODULES
EDV® DROPLET SEPARATORS
EDV® STACK
MAKEUP WATER
SLIPSTREAM TO PURGE TREATMENT UNIT

CLEAN GAS OUT

EDV® Scrubbing System
PFD w/LoTOx
(Only Ozone Injection added)
<table>
<thead>
<tr>
<th>Application</th>
<th>Location</th>
<th>Capacity</th>
<th>NO\textsubscript{x} In / Out</th>
<th>Start-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Fired Boiler</td>
<td>Southern CA</td>
<td>400 HP</td>
<td>150-70-30 ppm / 2-5 ppm</td>
<td>1997</td>
</tr>
<tr>
<td>Gas Fired Boiler</td>
<td>Southern CA</td>
<td>1000 HP</td>
<td>30-40 ppm / 4 ppm</td>
<td>January '02</td>
</tr>
<tr>
<td>Coal Fired Power Plant</td>
<td>Ohio</td>
<td>25 MW</td>
<td>200 ppm / 10 ppm</td>
<td>October '01</td>
</tr>
<tr>
<td>SS Pickling Process</td>
<td>Pennsylvania</td>
<td>--</td>
<td>1000-3400 ppm / 100 ppm</td>
<td>February '00</td>
</tr>
<tr>
<td>Refinery FCCU-EDV w/ Integral LoTOx</td>
<td>Woods Cross, UT</td>
<td>9,000 bpsd</td>
<td>70-110 ppm / 20 ppm</td>
<td>October, '12</td>
</tr>
<tr>
<td>Refinery FCCU (Pre-Invested for LoTOx)</td>
<td>Arkansas</td>
<td>20,000 bpsd</td>
<td>70-100 ppm / 10 ppm</td>
<td>June, 2007</td>
</tr>
<tr>
<td>Refinery FCCU (Pre-Invested for LoTOx)</td>
<td>Ardmore, OK</td>
<td>40,000 bpsd</td>
<td></td>
<td>TBD</td>
</tr>
<tr>
<td>Refinery FCCU (Pre-Invested for LoTOx)</td>
<td>Three Rivers, TX</td>
<td>28,000 bpsd</td>
<td>70-110 ppm / 20 ppm</td>
<td>Oct. 2011</td>
</tr>
<tr>
<td>Refinery FCCU (Pre-Invested for LoTOx)</td>
<td>Placid Refining, LA</td>
<td>30,000 bpsd</td>
<td></td>
<td>TBD</td>
</tr>
<tr>
<td>Refinery FCCU (pre-invested for LoTOx)</td>
<td>Alliance – Thailand</td>
<td>40,000 bpsd</td>
<td>90-165 ppm / 10 ppm</td>
<td>TBD</td>
</tr>
<tr>
<td>Sulfuric Acid Regeneration with LoTOx</td>
<td>Linden, NJ</td>
<td>80,000 lbs/hr</td>
<td></td>
<td>1st Quarter '08</td>
</tr>
<tr>
<td>Refinery FCCU-LoTOx retrofit to ext. EDV</td>
<td>Texas City, TX</td>
<td>52,000 bpsd</td>
<td>70-100 ppm / 10 ppm</td>
<td>February, 2007</td>
</tr>
<tr>
<td>Refinery FCCU (Pre-Invested for LoTOx)</td>
<td>El Dorado, KS</td>
<td>40,000 bpsd</td>
<td>150 ppm / 20 ppm</td>
<td>TBD</td>
</tr>
<tr>
<td>Refinery FCCU-EDV w/ Integral LoTOx</td>
<td>Houston, TX</td>
<td>58,000 bpsd</td>
<td>100-150 ppm / 10 ppm</td>
<td>April, 2007</td>
</tr>
<tr>
<td>Refinery FCCU LoTOx retrofit to ext. EDV</td>
<td>Texas City, TX</td>
<td>60,000 bpsd</td>
<td>100-150 ppm / 8 ppm</td>
<td>Dec, 2007</td>
</tr>
<tr>
<td>Refinery FCCU-EDV w/ Integral LoTOx</td>
<td>Texas City, TX</td>
<td>130,000 bpsd</td>
<td>100-200 ppm / 10 ppm</td>
<td>July, 2007</td>
</tr>
<tr>
<td>Refinery FCCU-EDV w/ Integral LoTOx</td>
<td>St. Charles, LA</td>
<td>75,000 bpsd</td>
<td>75-100 ppm / 20 ppm</td>
<td>Nov, 2010</td>
</tr>
<tr>
<td>Refinery FCCU-EDV w/ Integral LoTOx</td>
<td>Corpus Christi, TX</td>
<td>45,000 bpsd</td>
<td></td>
<td>October, 2010</td>
</tr>
</tbody>
</table>
EDV Wet Scrubbing Performance
In a Single Process Unit

Typical Emission Values:
Particulate - Less than 50mg/Nm3
SO2 - Less than 20ppm
SO3 - 80% removal plus
NOx - Less than 20/10ppm

Performance values based on over 75 operating Refinery Industry applications
Thank You

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