Wet Scrubbing Control Technology For FCCU's Particulate, SO_2 , SO_3 and NO_x Removal In One Process Unit

Garrett Billemeyer - Belco Technologies Corp.

BELCO® - Providing Proven Technologies

- EDV® Wet Scrubbing Systems
- Linde/BOC's LoTOx NOx Reduction Process

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(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
  - Conoco Phillips (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, Hyudai
  - 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 ?

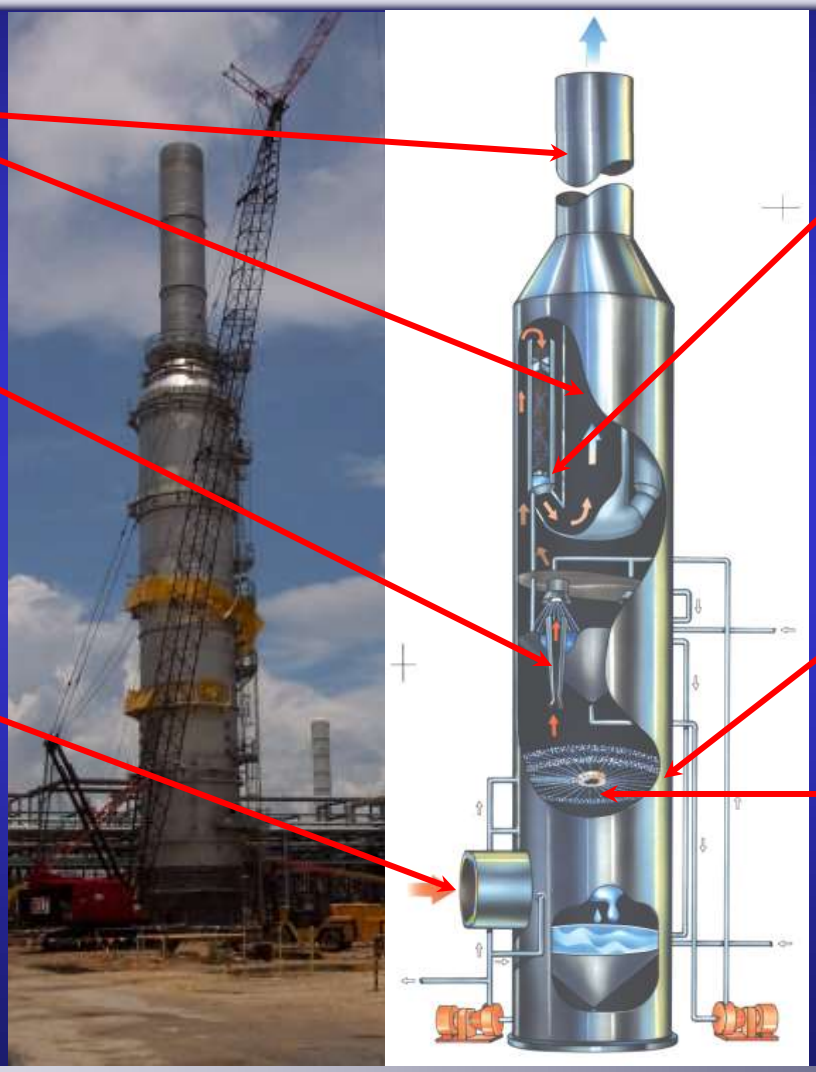
- High Collection Efficiency for Particulate, SO_X and now NO_X all in one step
- Proven Design Features for >5+ Year "Non-Stop" Operation
- Proven Capability to Handle FCC Upsets/Reversals
  - *Very High Particulate Carry Over*
  - *High Temperature Excursions (& COB Bypass)*
- Proven Capability to 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

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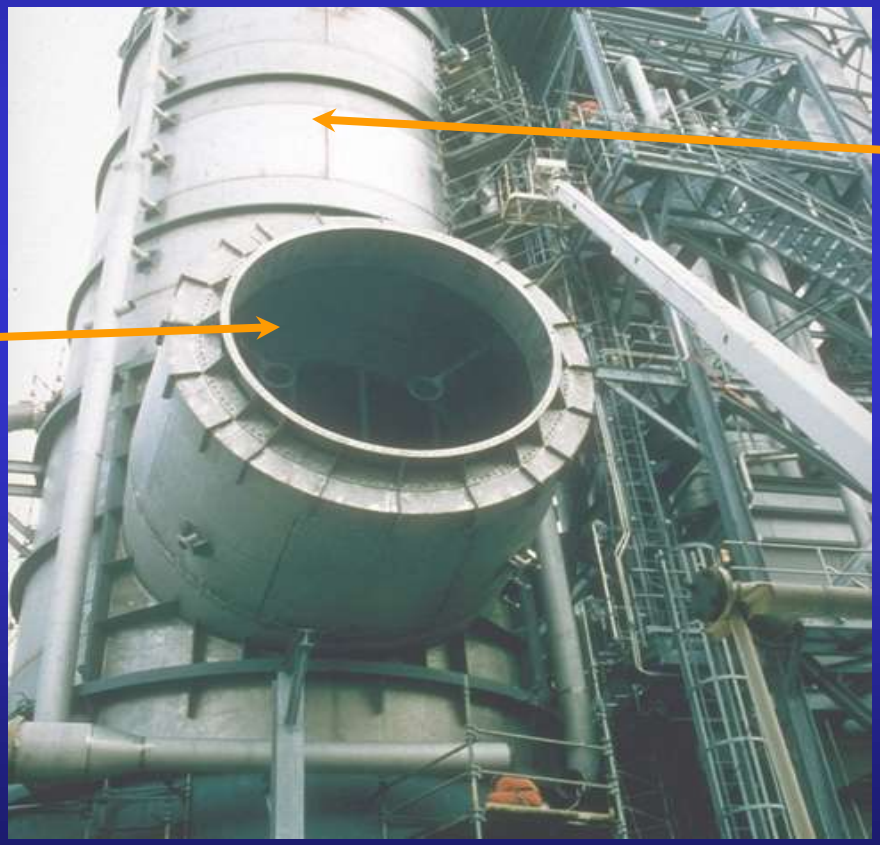
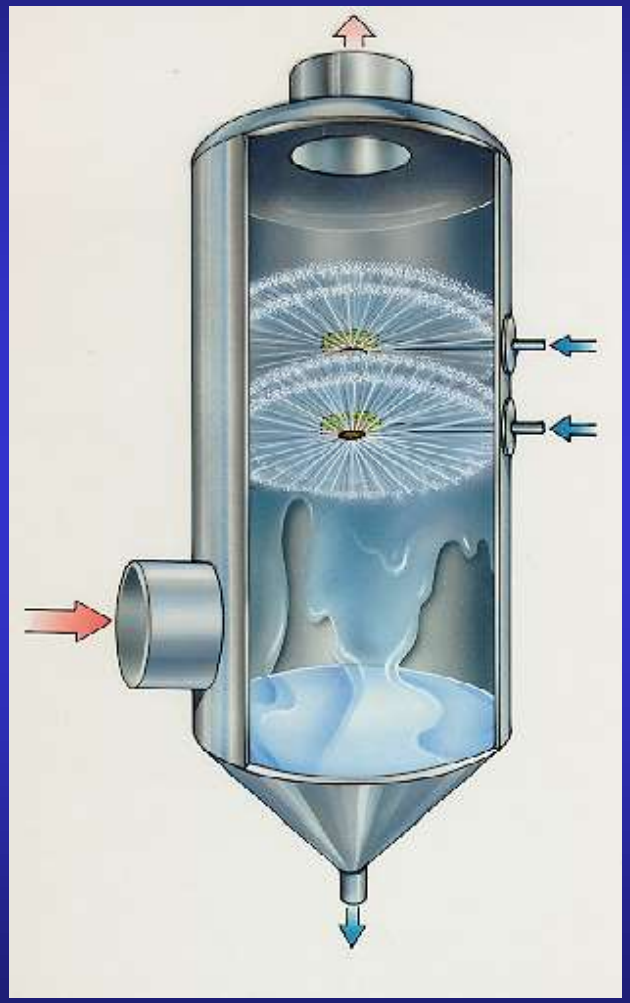
EDV® Wet Scrubbing
Quench & Spray Tower

Quench Section



Absorber/Spray Tower Section

EDV® Wet Scrubbing
Spray Tower



- Coarse PM, SO_2 & SO3 (plus NO_x when LoTOx™ is applied)
  - High Liquid / Gas Contact
    Cross Sectional Dense Water/Caustic Curtains
    SO2 & NOx Absorption/PM &SO3 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)

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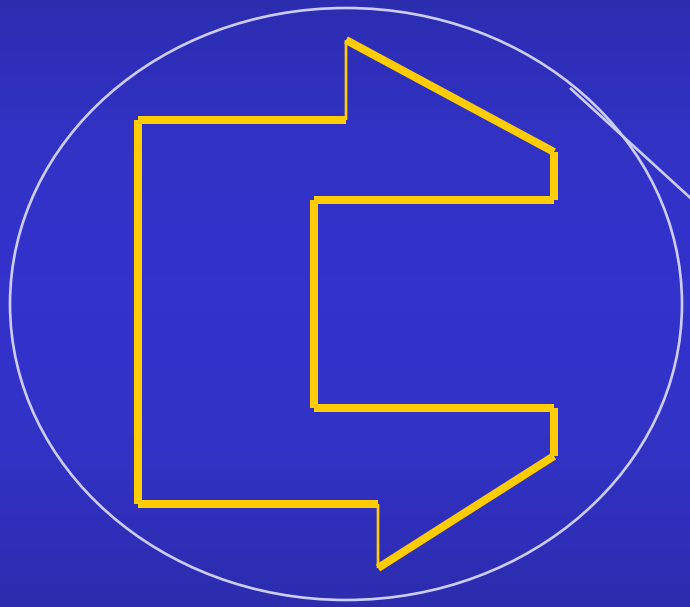
EDV® Wet Scrubbing

G® Nozzle

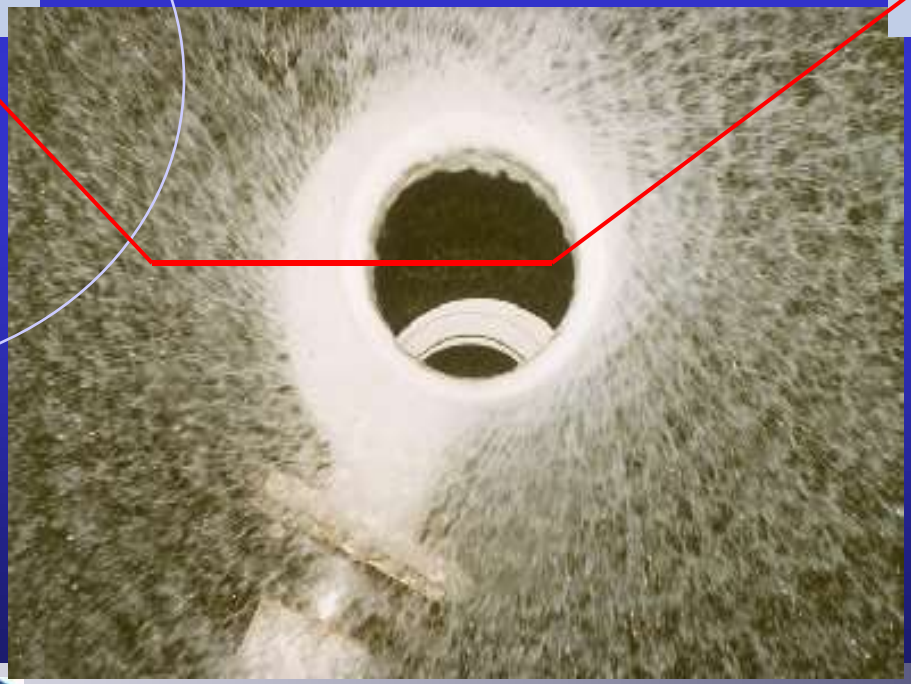


X -Section

EDV® Wet Scrubbing

(G®-400 Nozzle) Cross Section

Creates a Dual Reagent Spray by means of a Declining Trough Design



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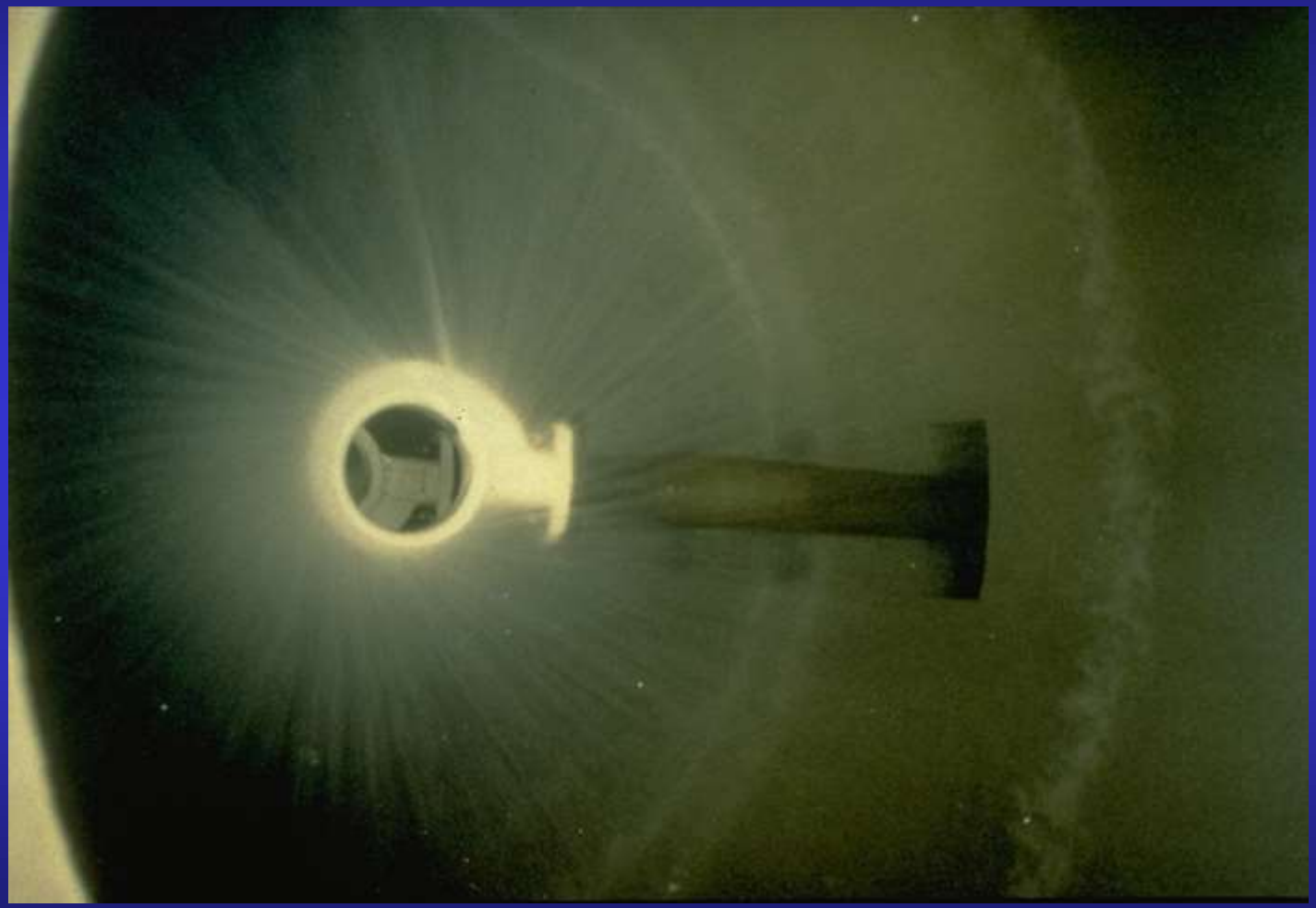
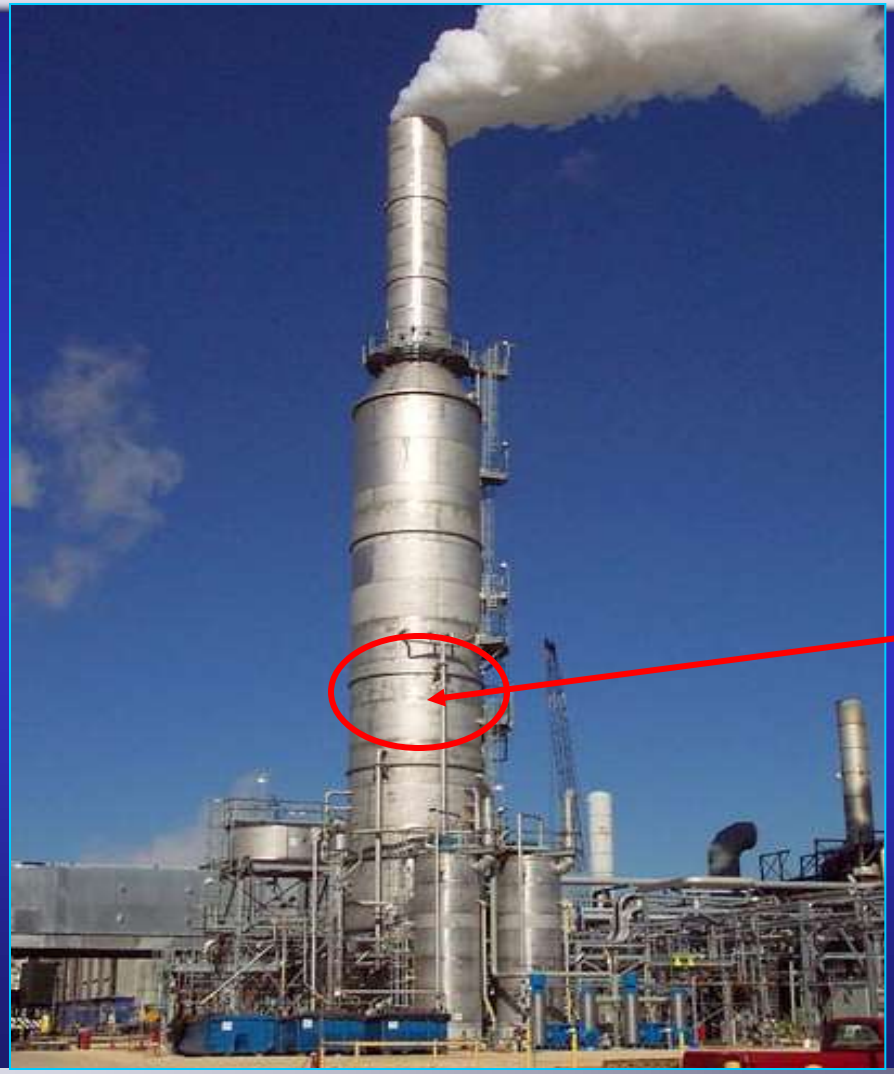
Single G® Nozzle Operation



EDV® Wet Scrubbing

Filtering Modules

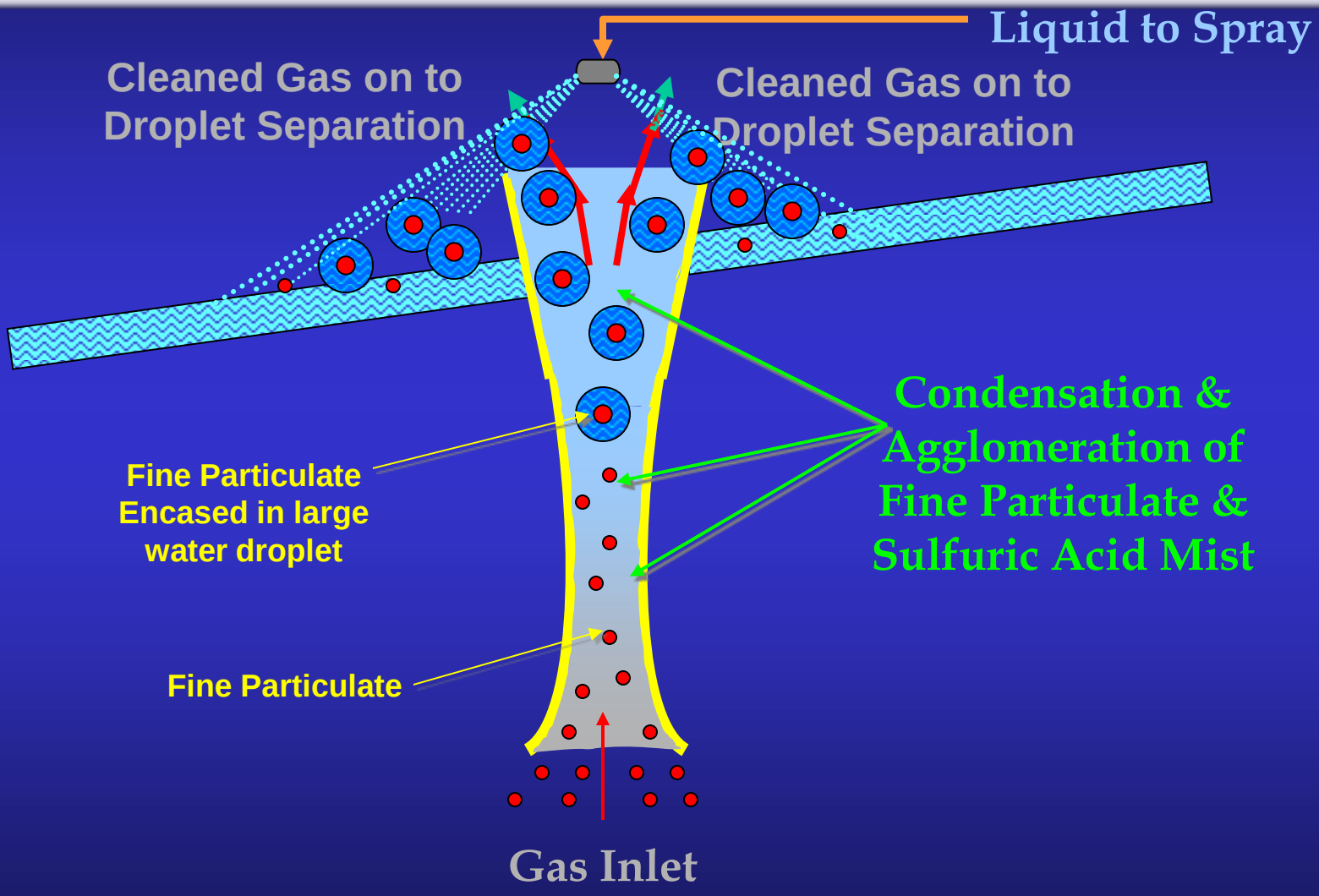


EDV® Filtering Module
Condensation & Filtration

- 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

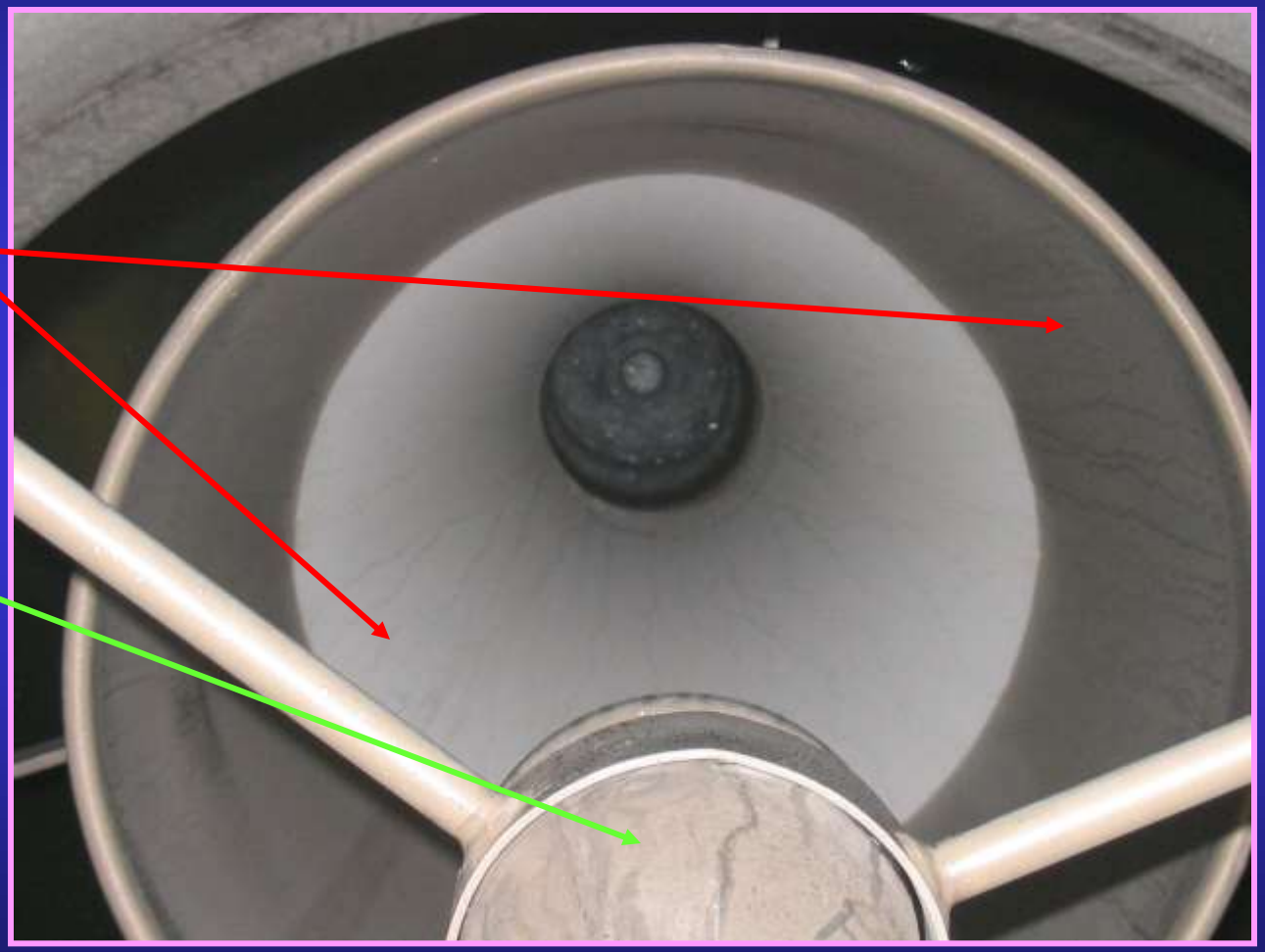
EDV® 5000 Filtering Module

Efficient Fine Particulate Control



EDV® 5000 Filtering Module

F-130 Spray Nozzle



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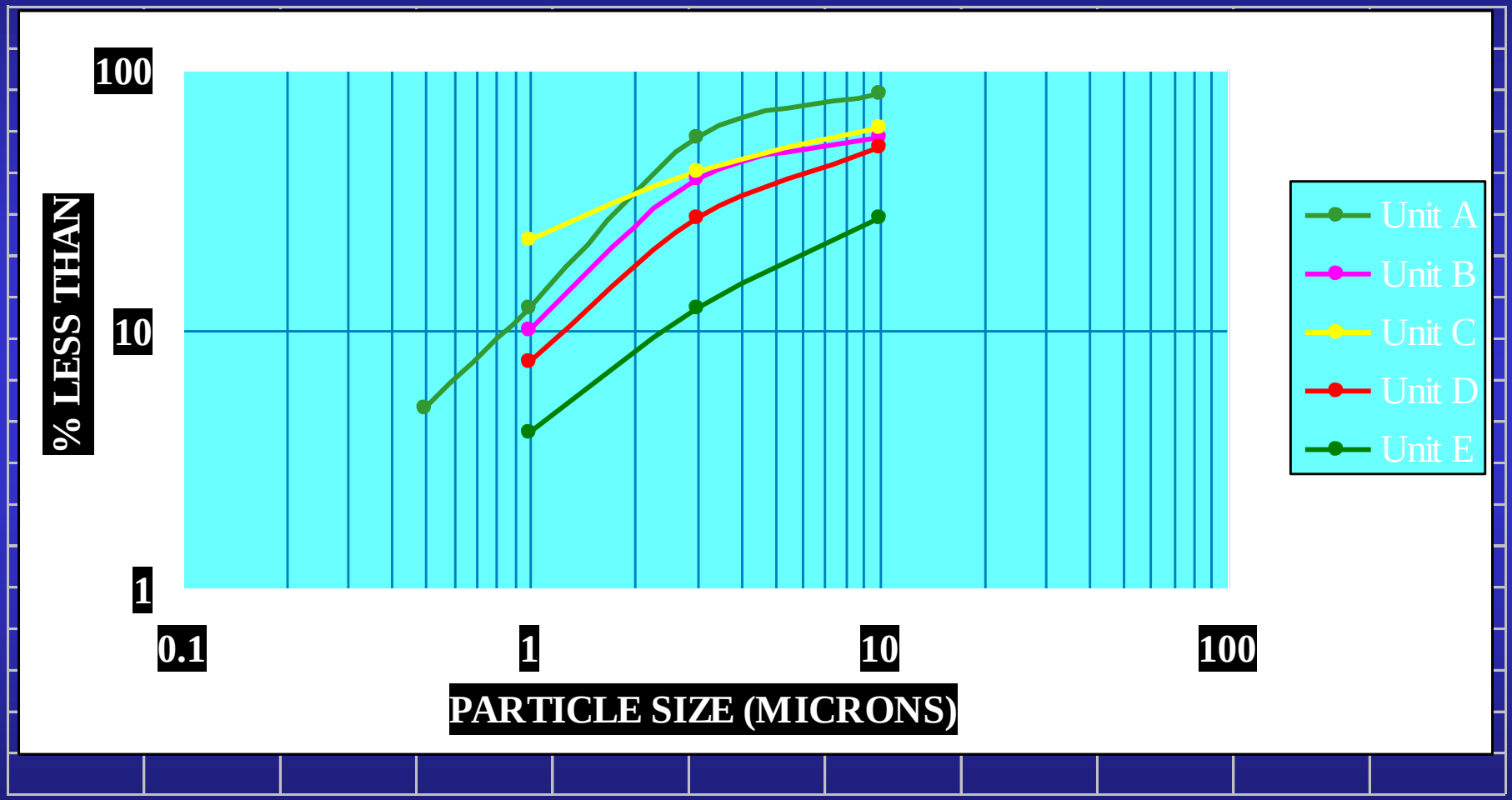
EDV® Wet Scrubbing

Particulate Control/Size Distribution



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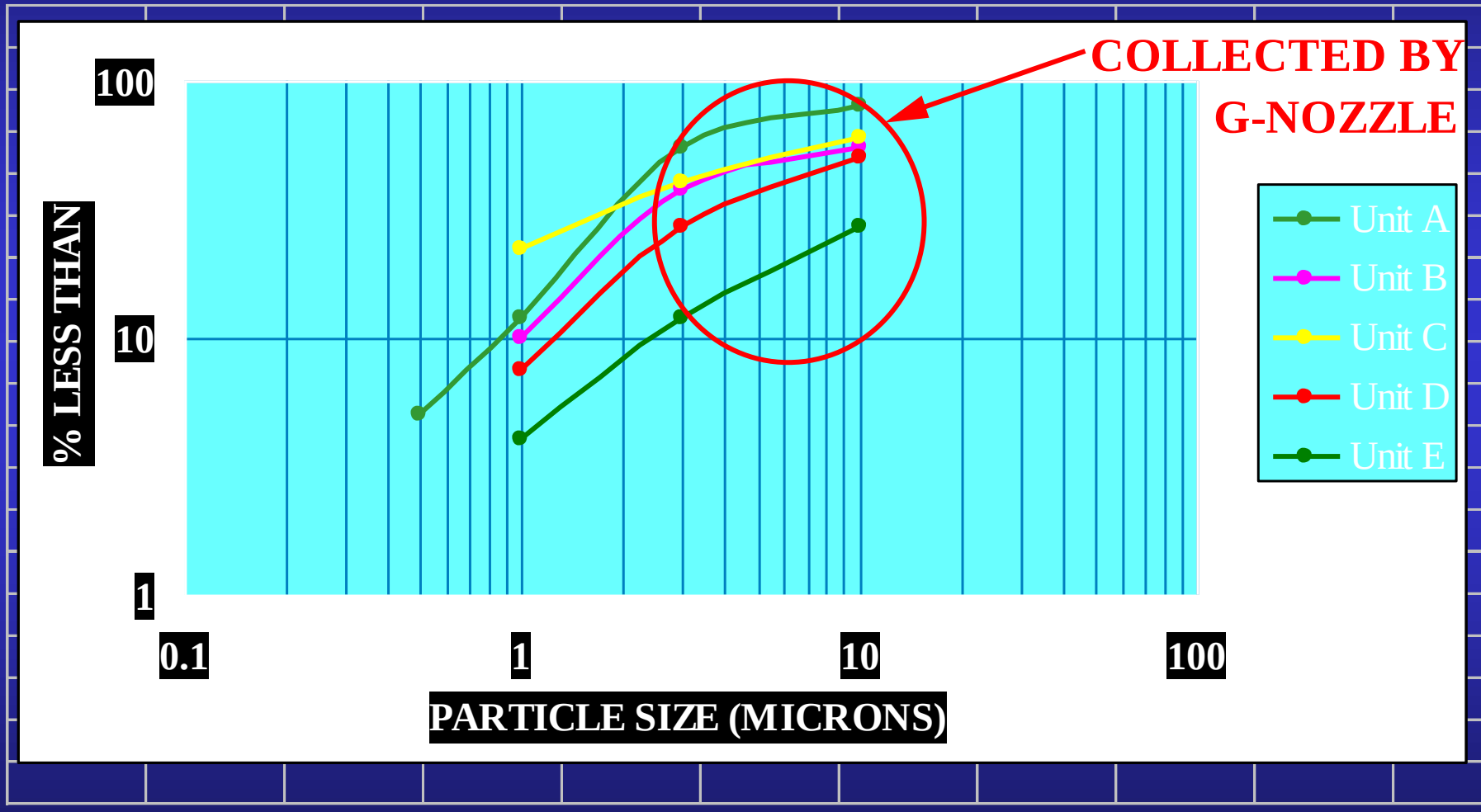
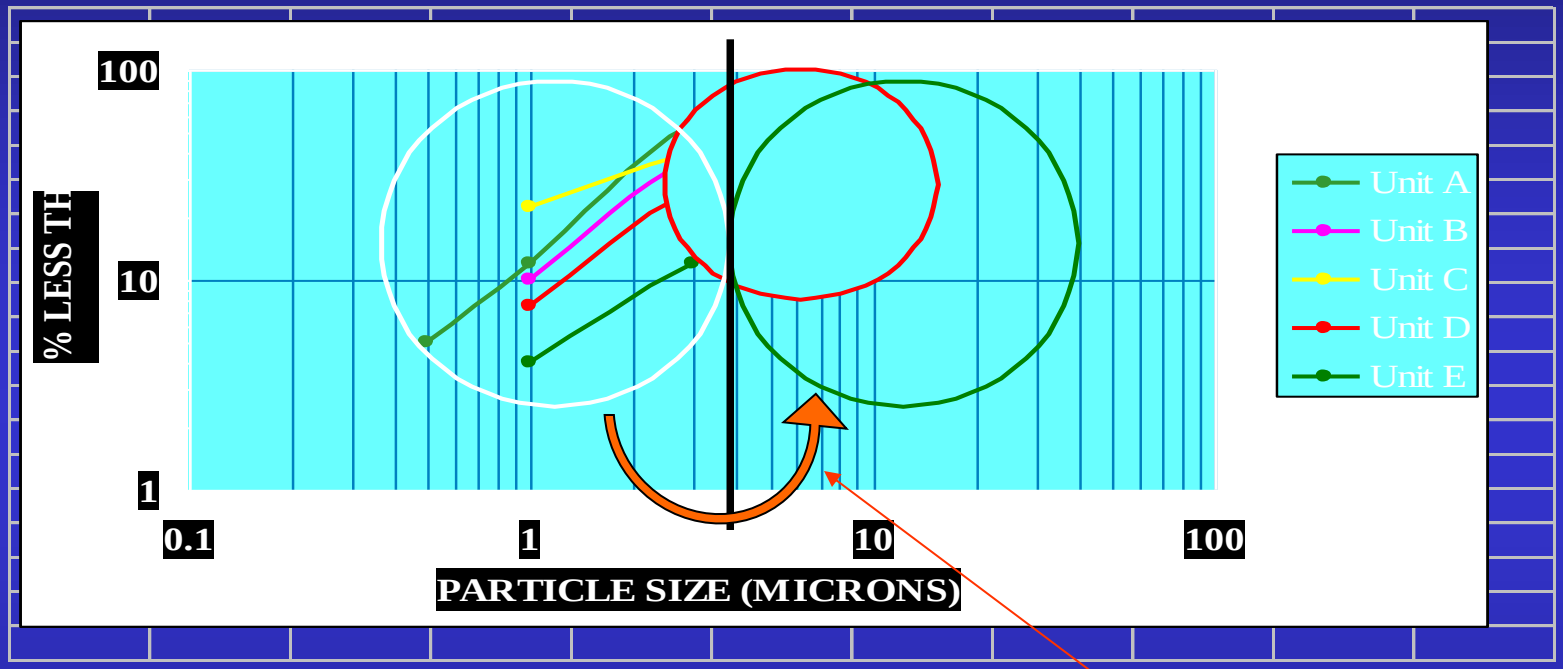
EDV® Wet Scrubbing

Particulate Control/Absorber G-Nozzle Collection



EDV® Wet Scrubbing System

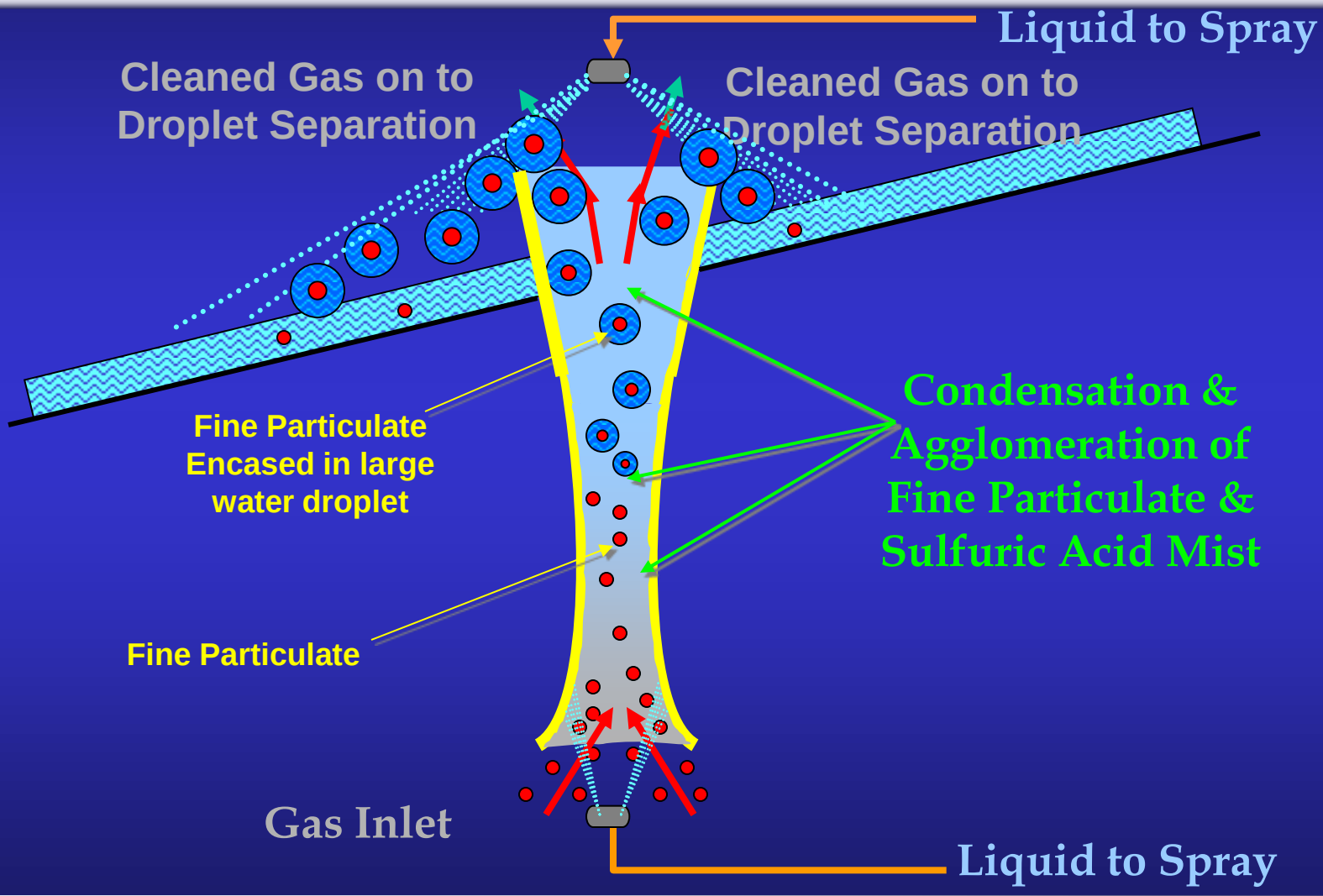
Particulate Control/Filter Module F-Nozzle Collection



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



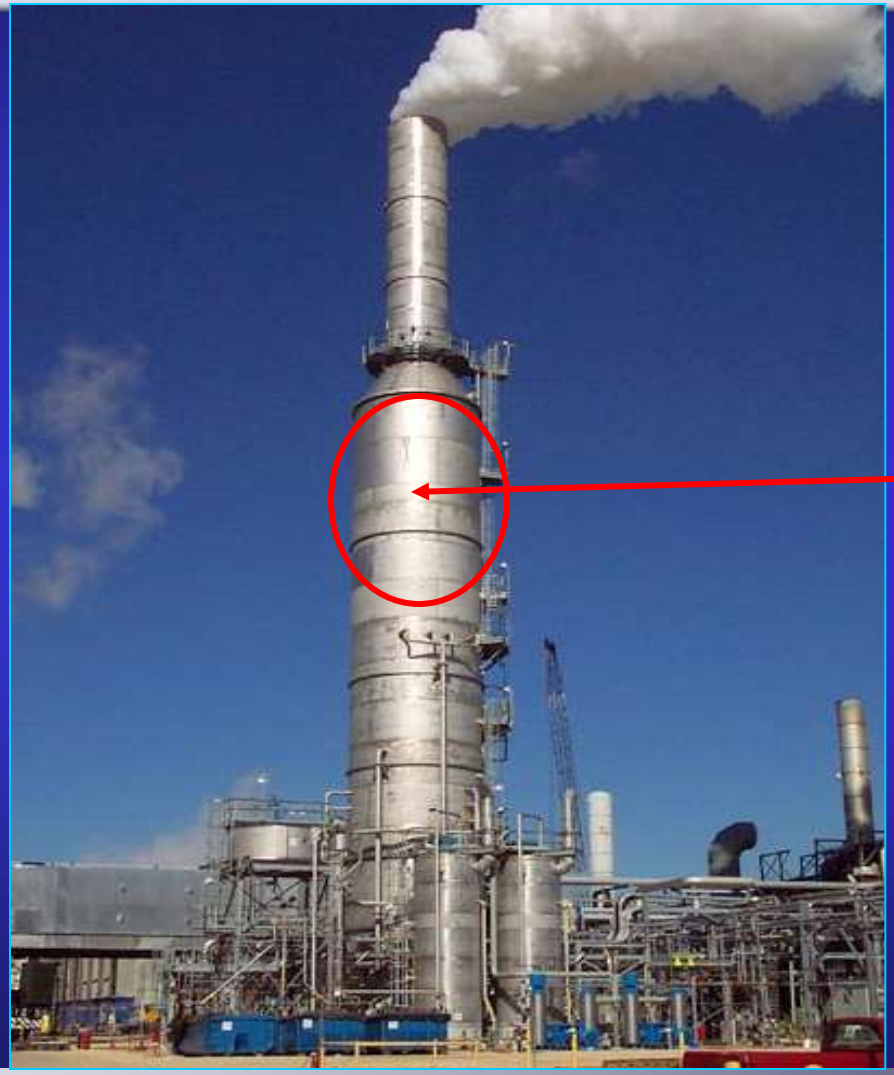
Filtering Modules

EDV® Wet Scrubbing

Removal of Excess Water Droplets without mist eliminators

EDV® Wet Scrubbing

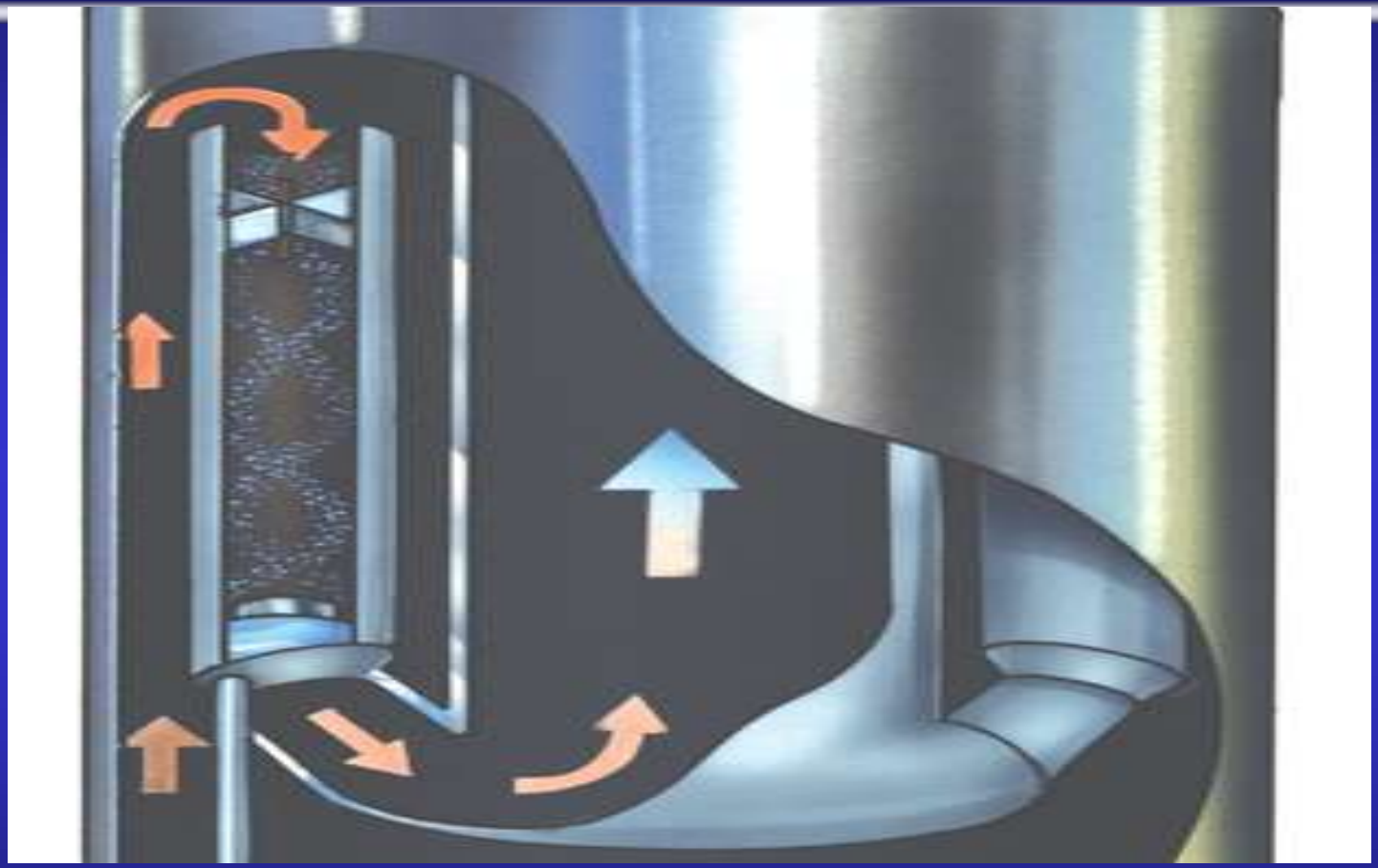
Droplet Separators



EDV® Droplet Separator

- Removes Droplets Carryover From Gas Stream
- Low Pressure Drop
- Non-Plugging Design
- Open /Self Cleaning
- No Mists Eliminators
- No Moving Parts

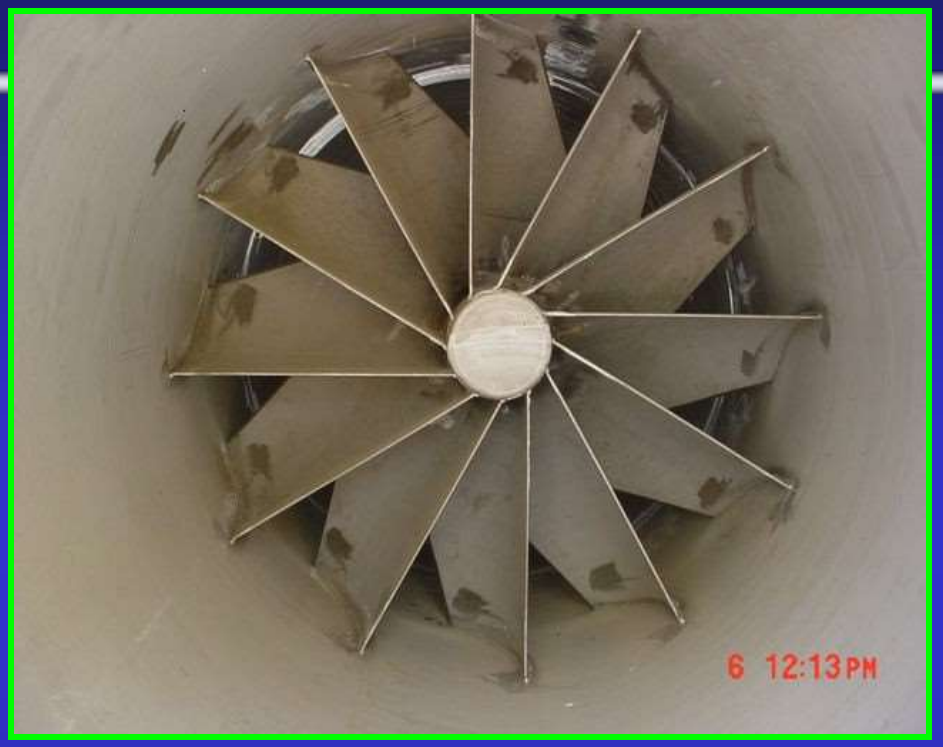
CYCLOLAB Droplet Separator



EDV® Wet Scrubbing System

Droplet Separators

CYCLOLAB Droplet Separator



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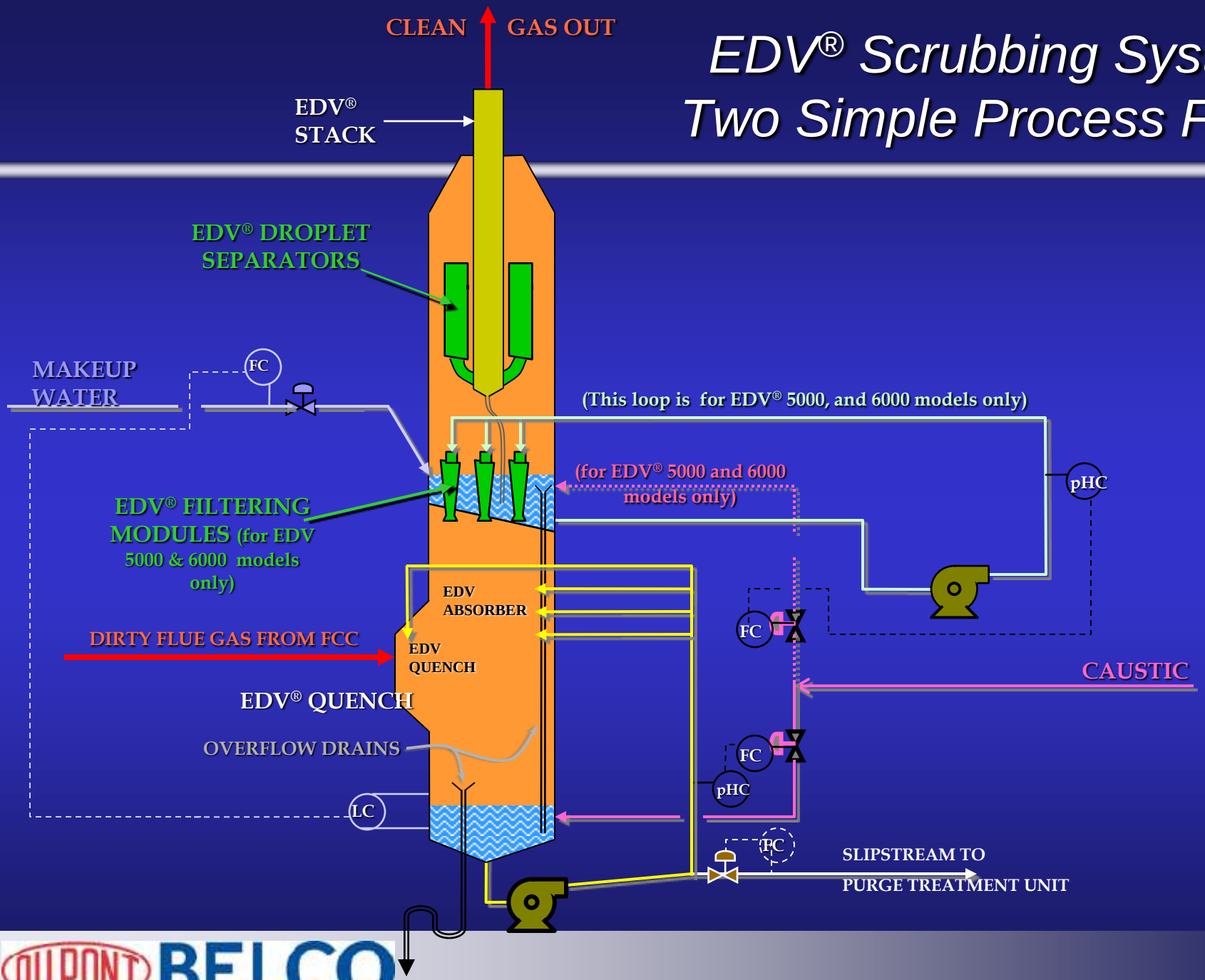
EDV® Scrubbing System
Two Simple Process Flows



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.

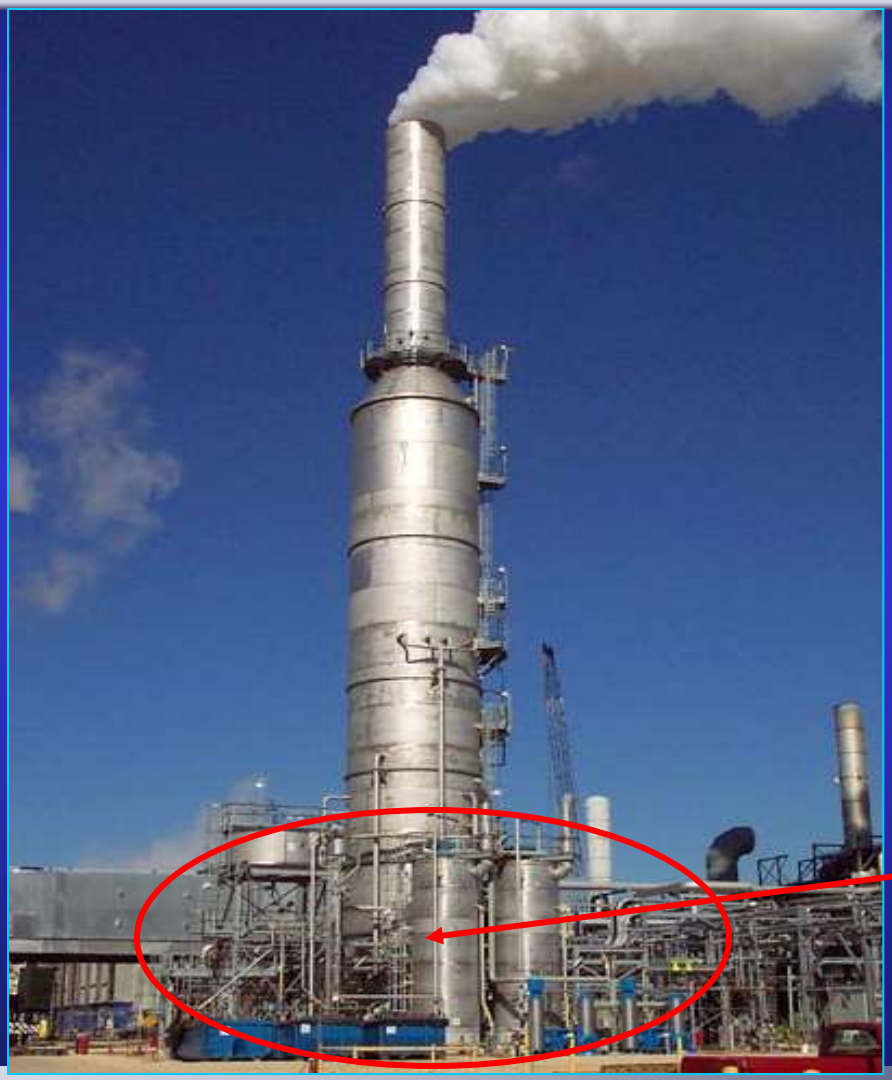
d) Monitor Delta ‘P’ for the Filtering Module Loop.

e) Monitor Clarifier Sludge Build-up

Treatment of Scrubber Purge

EDV® Wet Scrubbing

Purge Treatment Unit



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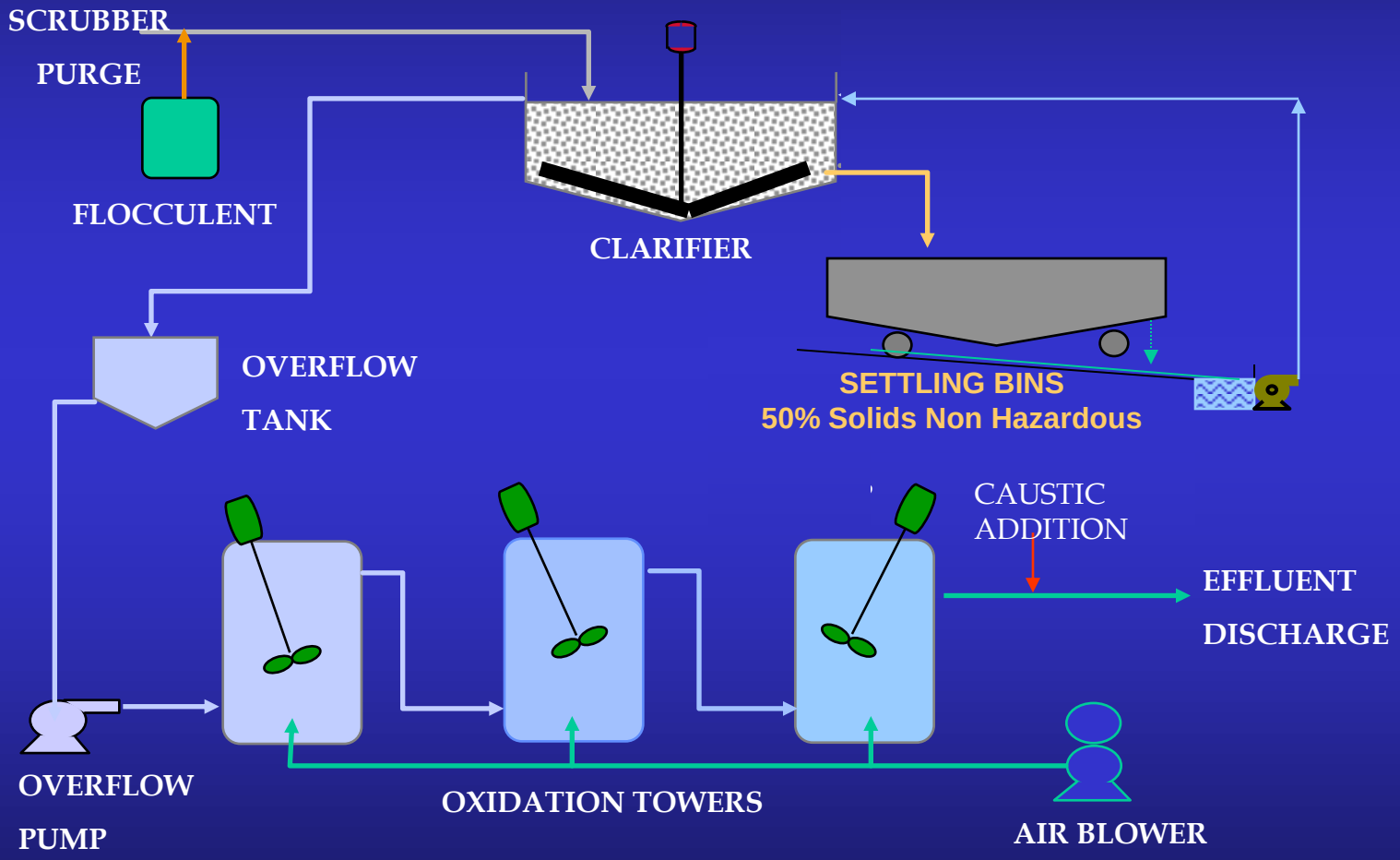
Typ. Purge Treatment Unit - PFD with Settling Bin

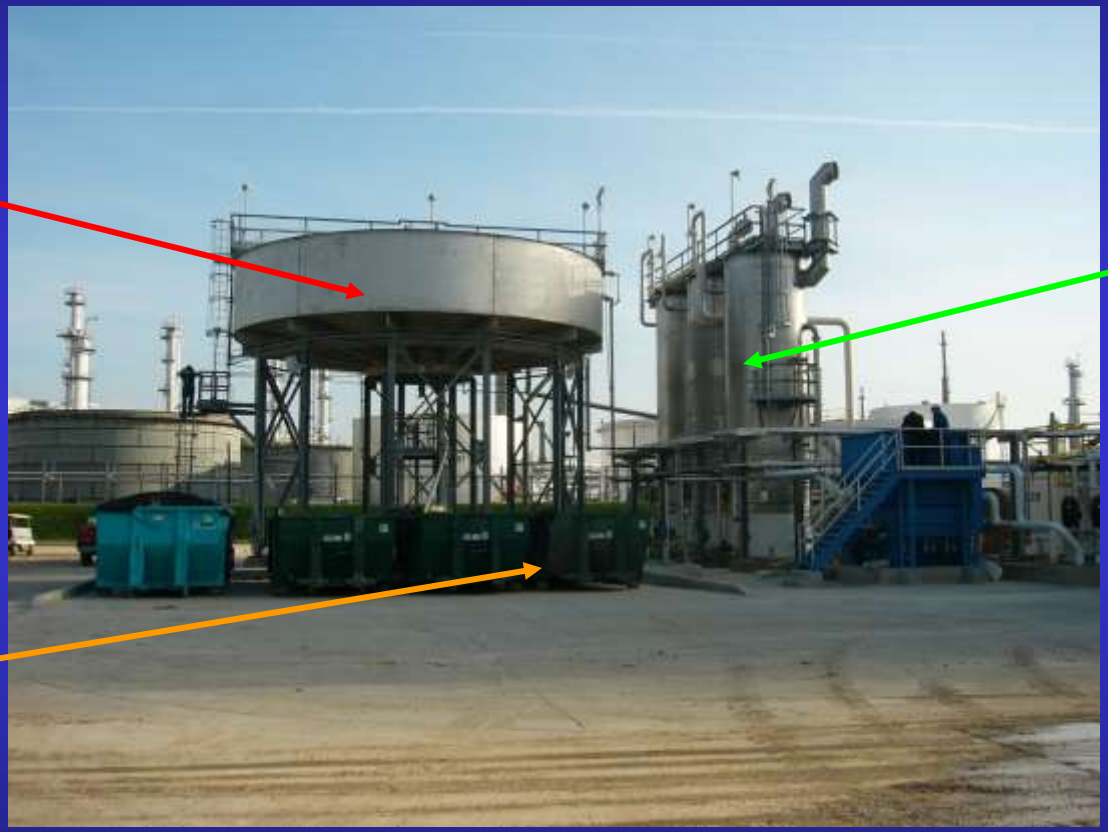


EDV® Wet Scrubbing System

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



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
-

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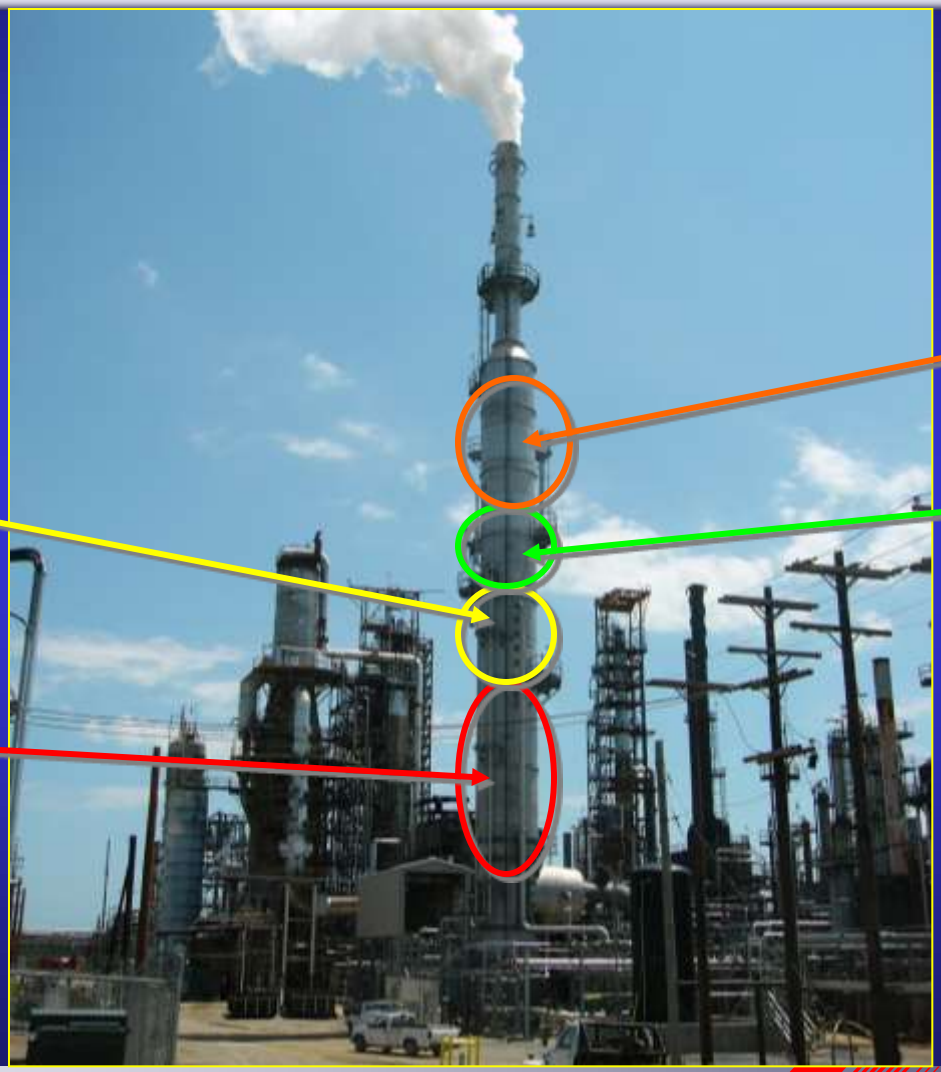
LoTO$_x$™ Installation on an FCCU

EDV® Wet Scrubber with LoTO$_x$™



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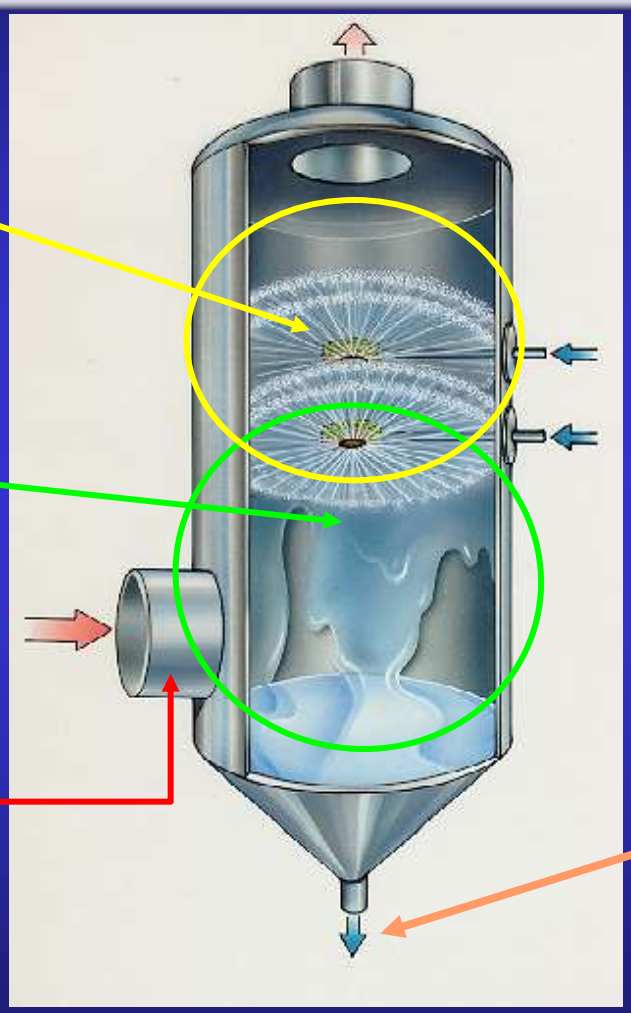
EDV® Wet Scrubbing System With LoTOx™ injection

N_2O_5 Conversion to HNO_3 and Scrubbing by EDV Nozzles

NO, NO_x Conversion to N_2O_5

Ozone Injection



- Ozone Injection after Quench
- Conversion to N_2O_5
- Conversion to Nitric Acid
- Conversion to Sodium Nitrate by contact with scrubber reagent
- Nitrates removed with Scrubber Purge

EDV® Wet Scrubbing System With LoTOx™ injection

Simplified LoTOx™ Chemistry

↑ $NO + O_3 \rightarrow NO_2 + O_2$

↑ $2NO_2 + O_3 \rightarrow N_2O_5 + O_2$

↑ $N_2O_5 + H_2O \rightarrow 2\ HNO_3$

↑ $HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$

Rate of Reaction

Low Temperature Oxidation of NOx:

Rate (k) = cm^3/molecule/sec
(298 degrees K)

$NO + O_3 \rightarrow NO_2 + O_2$		$k = 1.8 \times 10^{-14}$
$2\,NO_2 + O_3 \rightarrow N_2O_5 + O_2$		$k = 3.5 \times 10^{-17}$

$CO + O_3 \rightarrow CO2 + O_2$		$k < 1.1 \times 10^{-21}$
$SO_2 + O_3 \rightarrow SO3 + O_2$		$k = 2.2 \times 10^{-22}$

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

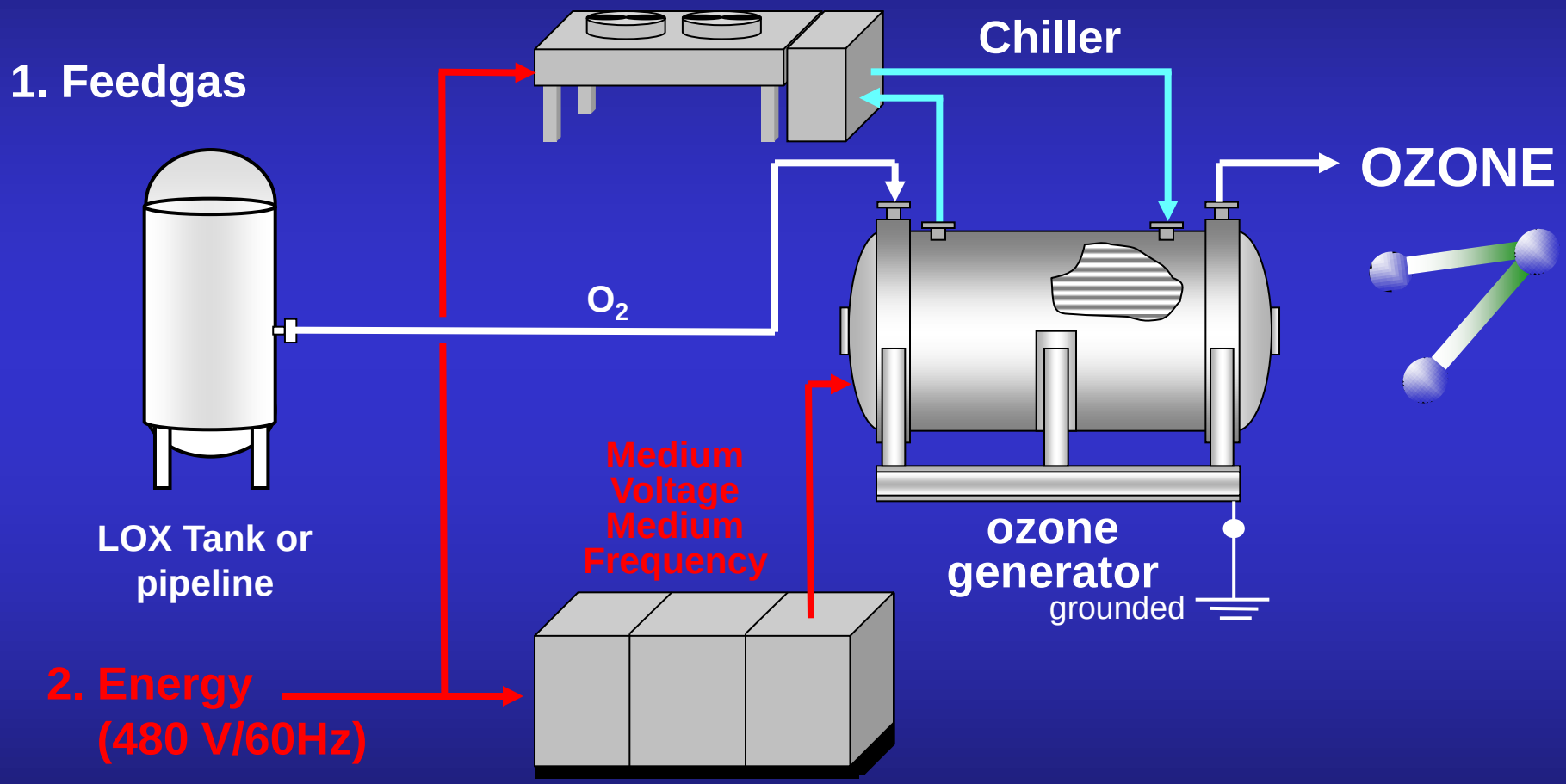
$N_2O_5 + H_2O \rightarrow 2\,HNO_3$ (Liquid Phase)

EDV® Wet Scrubbing System With LoTOx™ injection

Species	*Relative Solubility at 25 °C*
NO	1
NO_2	20
SO_2	2000
N_2O_5	>> 2000
HNO_3	Mixes with water in all proportions

LoTOx™ Process

Ozone Generation

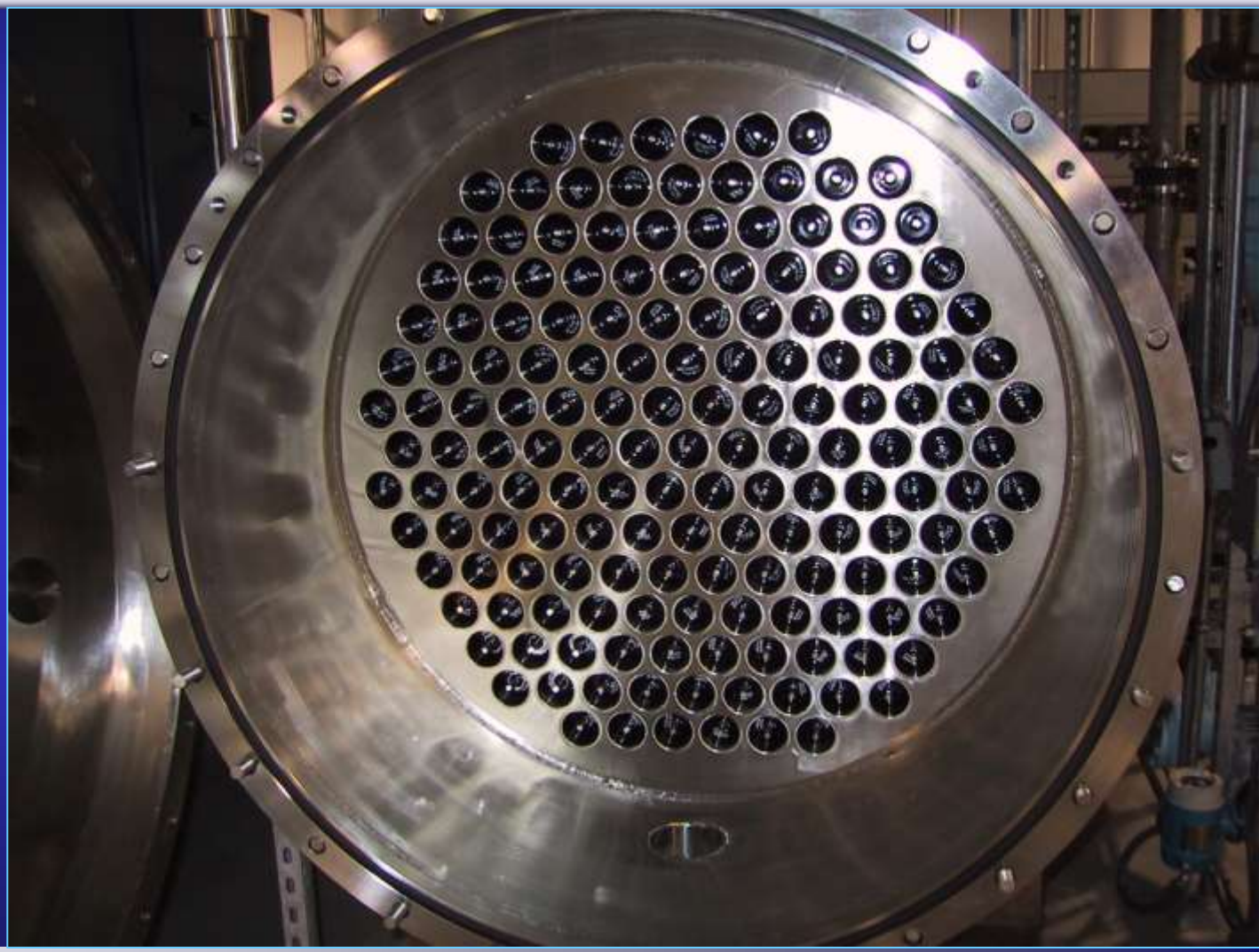


LoTOx™ Process

Ozone Generation

LoTOx™ Process
Ozone Generation

1370 Lbs/day OZONE GENERATOR - OZONE SIDE OPEN



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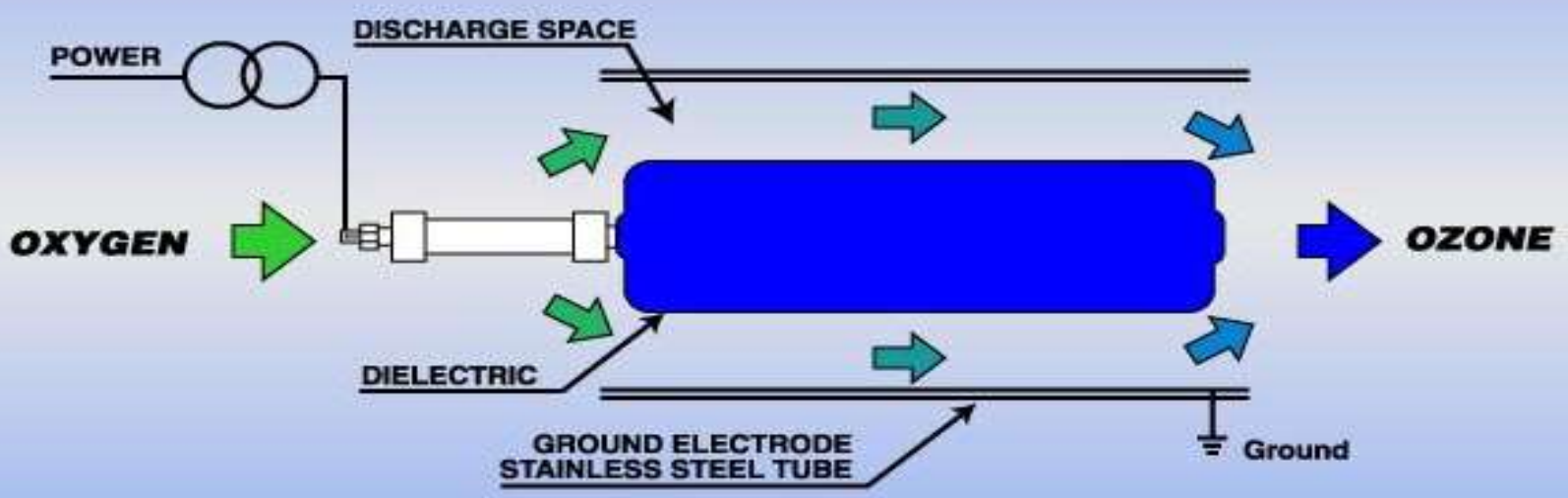
LoTOx™ Process

Ozone Generation

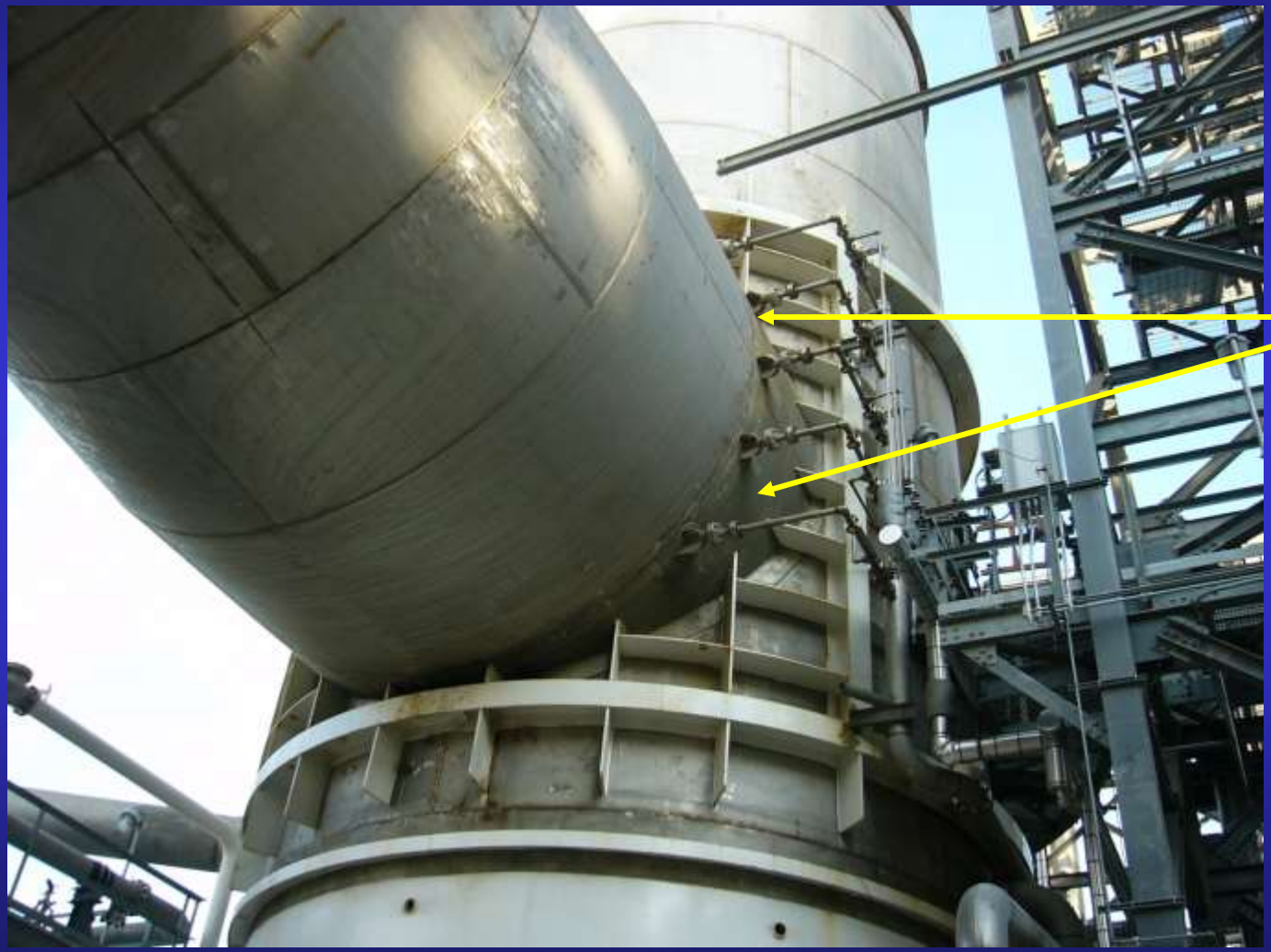
Single Ozone Generator Cell Dielectric



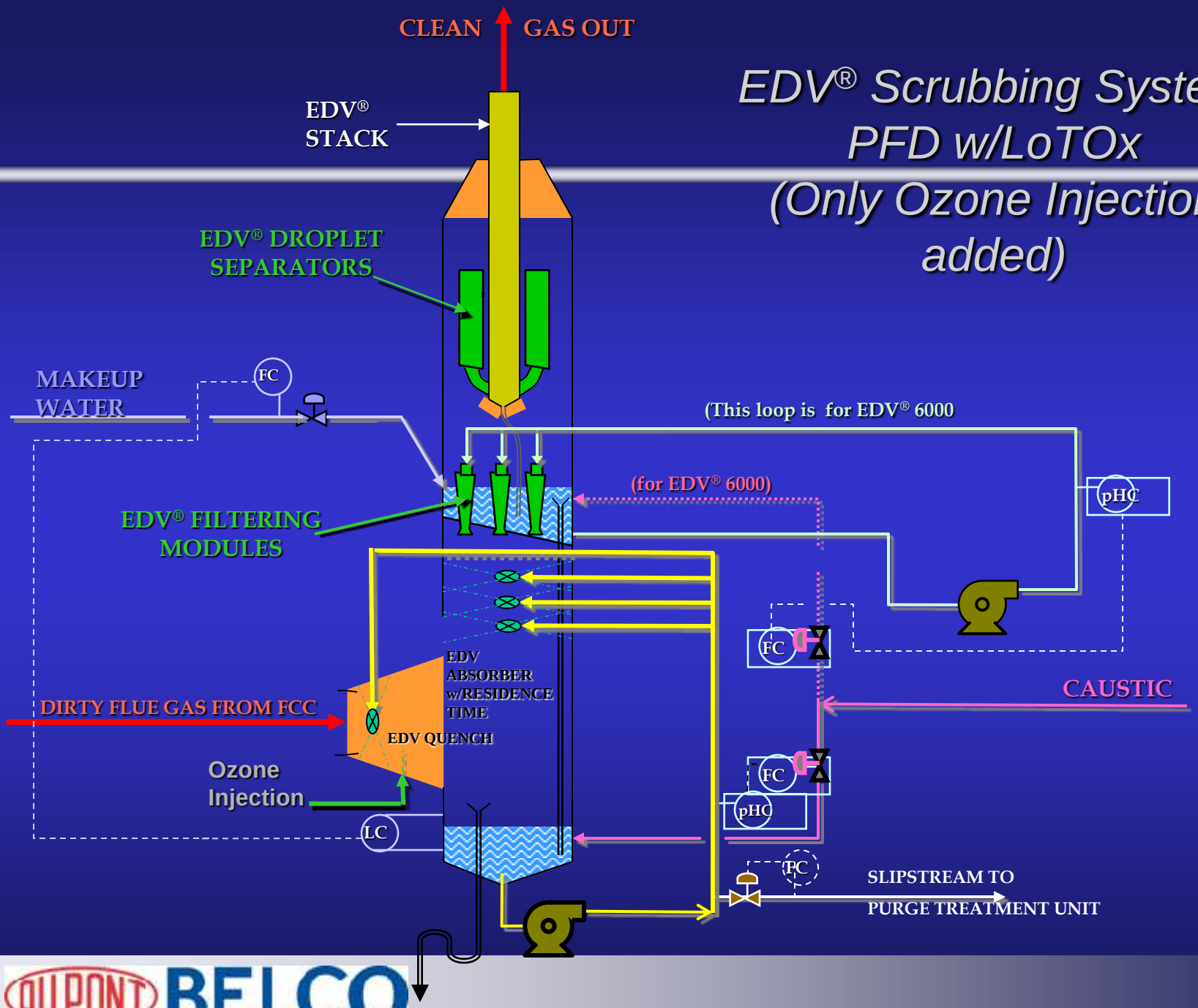
$$3\,O_2 \rightleftharpoons 2\,O_3$$

EDV® Wet Scrubbing System

Ozone Injection



EDV® Scrubbing System PFD w/LoTOx (Only Ozone Injection added)



LoTOx™

Partial List/Commercial Applications

Application	Location	Capacity	NO_x In / Out	Start-up
Gas Fired Boiler	Southern California	400 HP	150-70-30ppm / 2-5ppm	1997
Gas Fired Boiler	Southern California	1000 HP	30-40ppm / 4ppm	January '02
Coal Fired Power Plant	Ohio	25 MW	200ppm / 10ppm	October '01
SS Pickling Process	Pennsylvania	--	1000-3400ppm100ppm	February '00
Refinery FCCU-EDV w/ Integral LoTOx	Woods Cross, UT	9,000 bpsd	70-110ppm / 20ppm	October, '12
Refinery FCCU (Pre-Invested for LoTOx)	Arkansas	20,000 bpsd	**70-100ppm/10ppm**	**June, 2007**
Refinery FCCU (Pre-Invested for LoTOx)	Ardmore, Oklahoma	40,000 bpsd		**TBD**
Refinery FCCU (Pre-Invested for LoTOx)	Three Rivers, Texas	28,000 bpsd	**70-110ppm/20ppm**	**Oct. 2011**
Refinery FCCU (Pre-Invested for LoTOx)	Placid Refining, LA	30,000 bpsd	**90-165ppm/10ppm**	**TBD**
Refinery FCCU (pre-invested for LoTOx)	Alliance – Thailand	40,000 bpsd		**TBD**
Sulfuric Acid Regeneration with LoTOx	Linden, NJ	80,000lbs/hr		**1st Quarter '08**
Refinery FCCU-LoTOx retrofit to ext. EDV	Texas City, TX	52,000 bpsd	**70-100ppm/10ppm**	**February, 2007**
Refinery FCCU (Pre-Invested for LoTOx)	El Dorado, KS	40,000 bpsd	**150ppm/20ppm**	**TBD**
Refinery FCCU-EDV w/ Integral LoTOx	Houston, TX	58,000 bpsd	**100-150ppm/10ppm**	**April, 2007**
Refinery FCCU LoTOx retrofit to ext. EDV	Texas City, TX	60,000 bpsd	**100-150ppm/8ppm**	**Dec. , 2007**
Refinery FCCU-EDV w/ Integral LoTOx **Refinery FCCU-EDV w/Integral LoTOx**	Texas City, TX St. Charles, LA	130,000 bpsd 75,000 bpsd	**100-200ppm/10ppm** **75-100ppm/20ppm**	**July, 2007** **Nov, 2010**

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

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Thank You

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