DECON TECHNOLOGY
ZYME FLOW®

Preparing for Bottom-of-the-Barrel Vessel Entry Venezuelan Coker Unit Emergency Shutdown

Dr. Steve. Matza – Chief Scientist

REFCOMM GALVESTON
MAY 8-12 2017

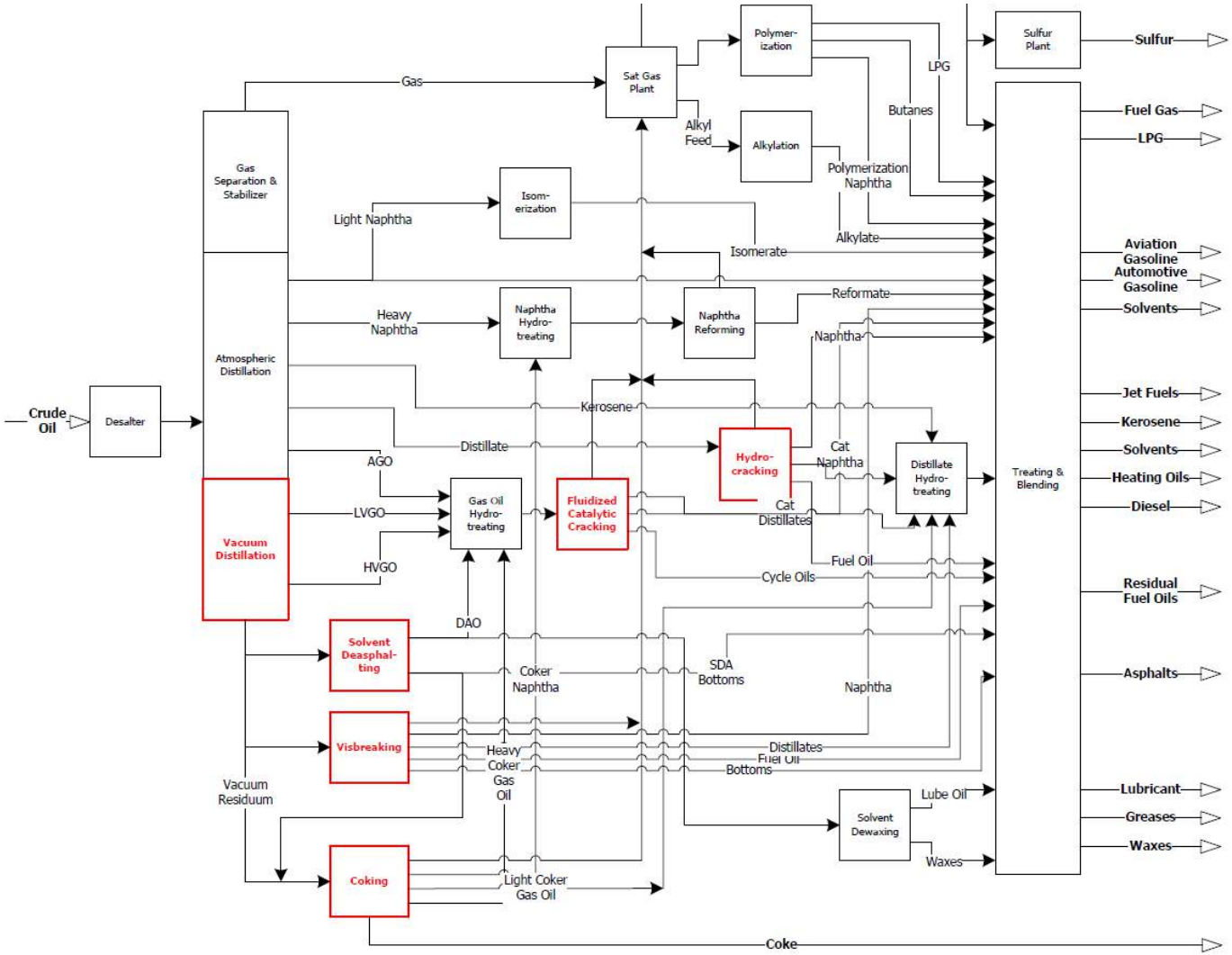
Bottom-of-the-Barrel Vessels

1. Bottom of the Barrel Background
2. Venezuela Coker TAR Case Study
3. Bottom-of-the-Barrel Cleaning Options
4. Bottom of the Barrel TAR Best Practice

DECON TECHNOLOGY
ZYME FLOW®

Where is the Bottom-of-the-Barrel?

- VDU
- Deasphalting
- Visbreaker
- Coker
- FCC
- Hydrocracker

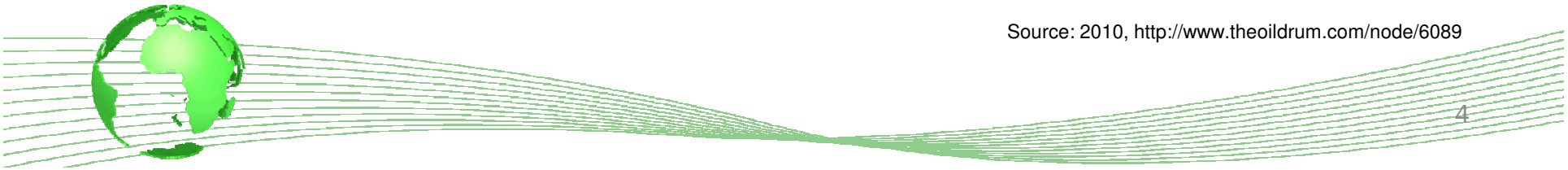


Source: 2016 John Jechura, Colorado School of Mines

DECON TECHNOLOGY ZYME FLOW®

What is Bottom of the Barrel?

Crude Fraction	Number of Carbons	Boiling Point (F)
Gas	1-4	<32
Light Naphtha	5-7	80-200
Heavy Naphtha	6-10	200-350
Kerosene	10-15	350-550
Light Gas Oil	13-18	400-650
Heavy Gas Oil	16-40	600-1050
Residuum	**>40**	**>1050**



Source: 2010, http://www.theoildrum.com/node/6089

DECON TECHNOLOGY
ZYME FLOW®

Case Study

Coker Unit Turnaround - Venezuela

Venezuela Coker Decontamination

Project

- Decontamination of the main fractionator coker column at a Venezuela refinery
- Main goal; eliminate delays in vessel entry by minimizing manual and mechanical cleaning activities of the tower

Challenge

- Large amounts of coke, H_2S, and pyrophoric concerns

DECON TECHNOLOGY
ZYME FLOW®

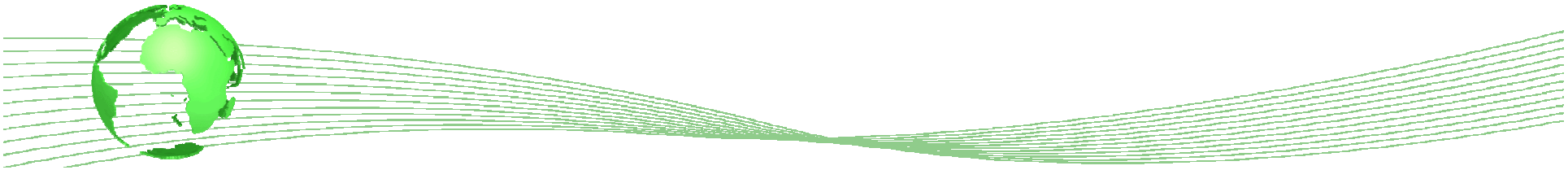
Venezuela Coker Decontamination

Past Procedure

- Traditional chemical cleaning every 4 years with 6 different hazardous chemicals requiring full body suits
- Chemicals circulated over an average of 36 hours
- Required 12 man crew per shift and 5 days of mechanical preparation

Past Procedure Results

- Left a tarry residue at the bottom of the tower up to 2 feet over the lower manway, completely burying bottom distributor
- Extensive mechanical cleaning was required under fresh air
- Leakage from chemical hoses required ground clean up
- Entry permits were delayed until all cleaning tasks were complete



DECON TECHNOLOGY ZYME FLOW®

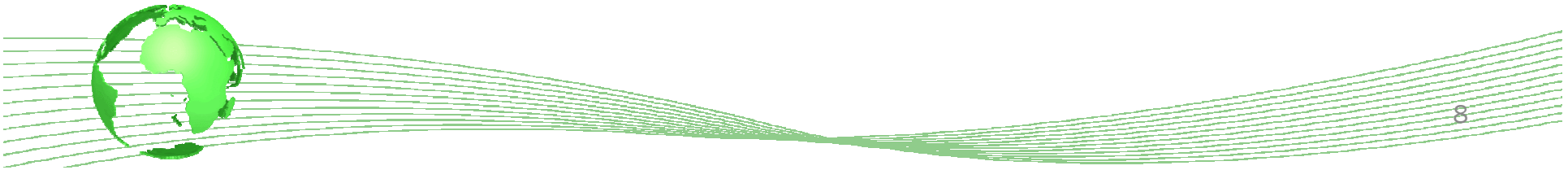
Traditional Cleaning Methods

Options

- Available refinery materials; BTX, heavy aromatic naphtha (HAN), gas oil, kerosene
- Chlorinated solvents
- Traditional/commodity chemicals; i.e. d-limonene
- Mechanical cleaning
- Mixed approach between methods

Results & Impacts

- Unpredictable results – often disappointing
- Removing value as feedstock (BTX)
- Long cleaning times
- High volume of waste
- Hazardous materials
- Multiple steps



Next Generation Best Practices

Rezyd-HP™ Cleaning Chemistry

ZymeFlow Decontamination Chemistry

Innovative Chemistry: Rezyd-HP

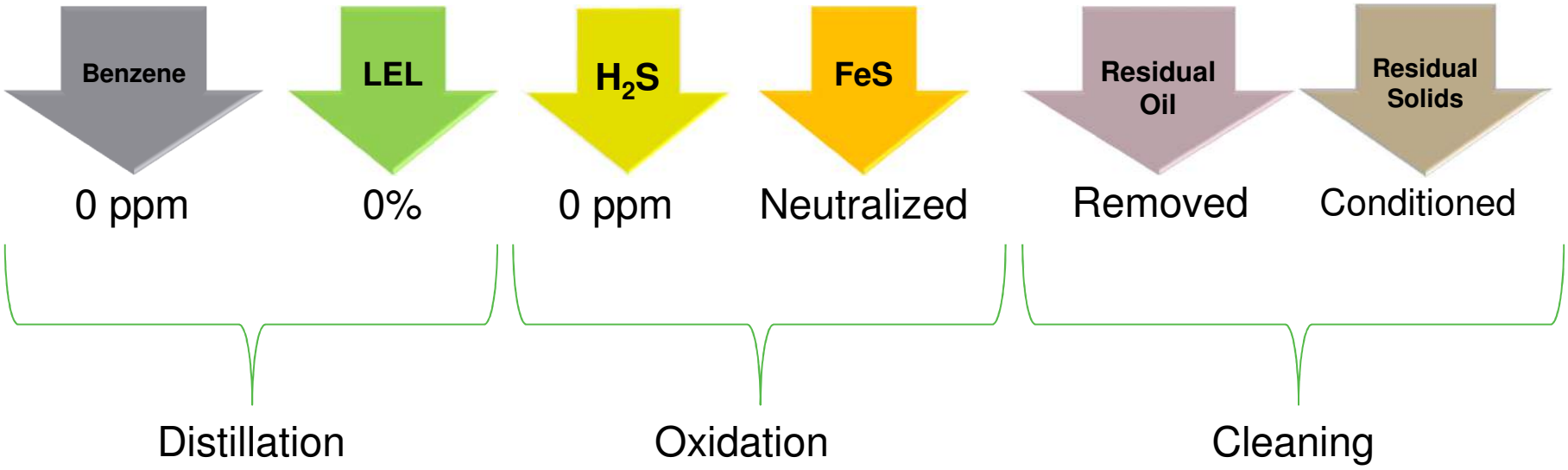
- Custom blend including high Kb solvent and surfactant
- Applied as an additive to common refinery cutter stocks
- Low hazard (2, 1, 0)
- Biodegradable
- Dissolves and/or fluidizes deposits
- Significantly decreases final cleaning and total cleaning time
- Low volumes required and less waste than other methods

Results: loose coke for ease of removal.
(Pictured: coker strainer basket)

ZymeFlow Decontamination

Preparing process units for safe entry in **8-12 hours**.

Simultaneous Treatment



Vapour-Phase® Decontamination Process

- Quickest possible entry into process equipment
- Operations shuts down and de-inventories equipment using standard procedures
- Zyme-Flow UN657 chemistry is injected into the equipment with steam
- Same boiling point as water therefore chemistry contacts all surfaces with minimum injection points

Vapour-Phase

Best Practice Approach

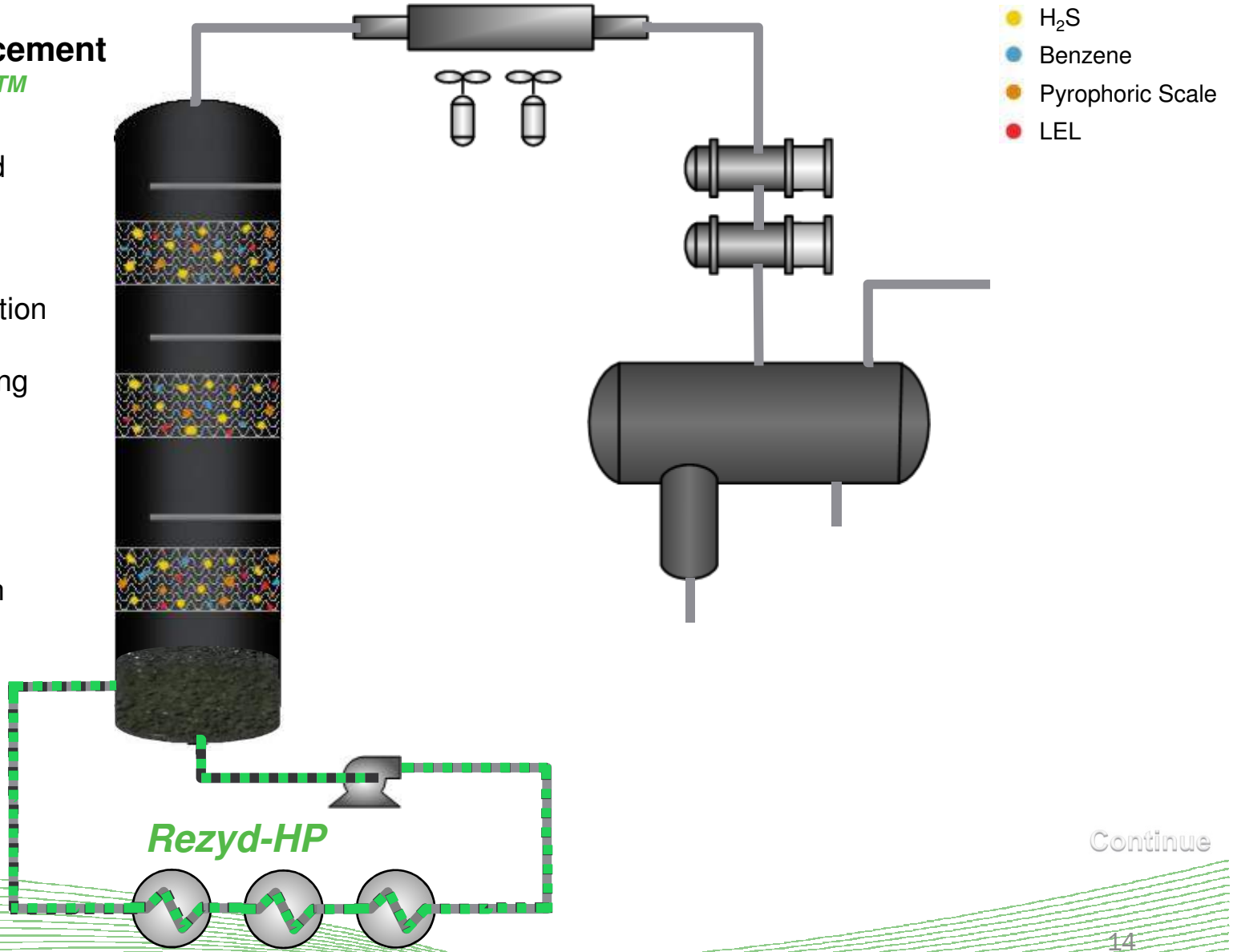
- Proprietary blended chemistry added to oil wash for much faster and more complete tower bottoms fluidization
- Entire tower system decontaminated simultaneously using boil out and Vapour-Phase®
- Additional treatments available for pyrophoric treatment on tower trays/packing

Asphalt sample (L), after Rezyd-HP (R)

Best Practice Bottom of the Barrel Unit

Oil Wash Enhancement Using *Rezyd-HP™*

- Unit is de-inventoried under standard plant procedures
- A cutter stock circulation is performed on the bottom circuit including exchangers
- ***Rezyd-HP*** added to enhance penetrating effect of the cutter stock, breaking down deposits within the circuit



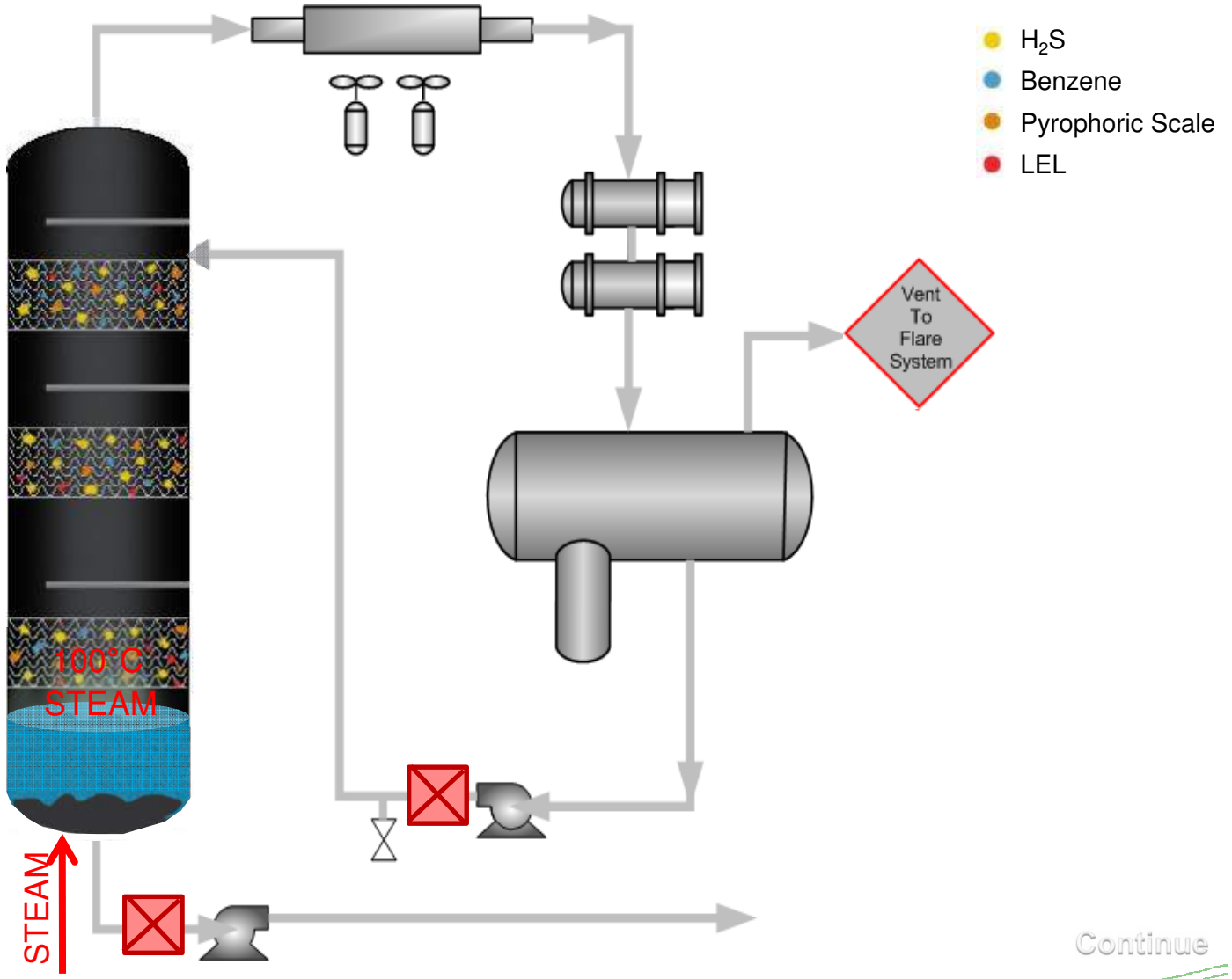
Continue

DECON TECHNOLOGY
ZYME FLOW®

Best Practice Bottom of the Barrel Unit

Boil Out with Vapour-Phase®

- Water is added to tower bottom (about 20% level)
- Steam injected into the bottom drain, or as close as possible
- ***Zyme-Flow®*** and ***Rezyd-X®*** added to water and temperature raised to above 100°C

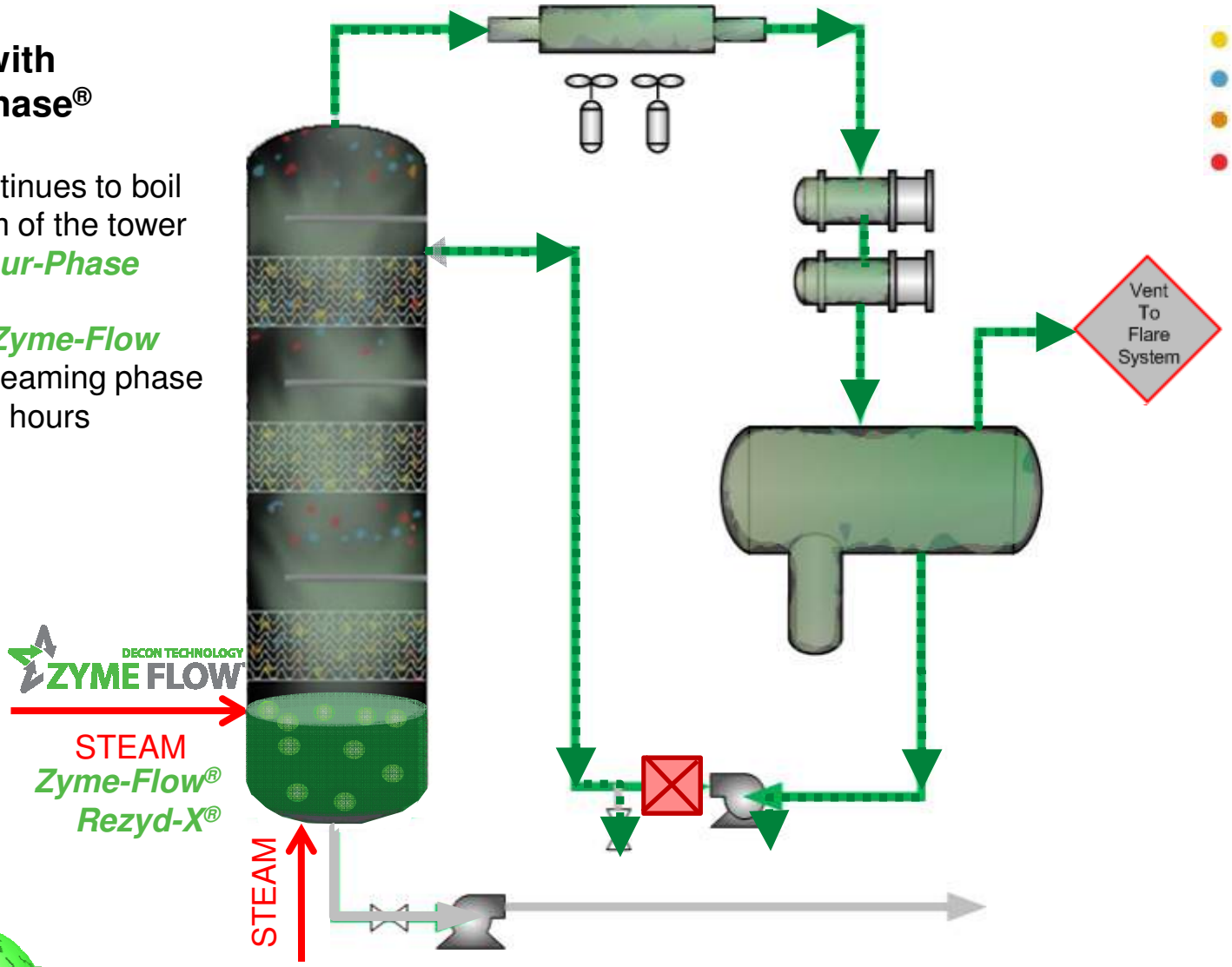


Continue

Best Practice Bottom of the Barrel Unit

Boil Out with Vapour-Phase®

- Solution continues to boil in the bottom of the tower during ***Vapour-Phase***
- Injection of ***Zyme-Flow*** during the steaming phase will last 8-12 hours



Continue

Best Practice Bottom of the Barrel

- Hardened deposits will be eliminated or loosened for ease of removal
- Greatly reduces mechanical work
- Trays and packing should be significantly easier to remove or repair
- Additional equipment can be segmented throughout production such as filter baskets, piping, and heat exchangers

VDU beds post treatment requiring no mechanical cleaning upon opening. (Pictured – VDU in EU.)

Venezuela Coker Engineered Solution

Bottoms Circulation

Specialty Rezyd-HP chemistry added to the HVGO cutter stock and circulated at the refinery's standard time and rate

Vapour-Phase® Application

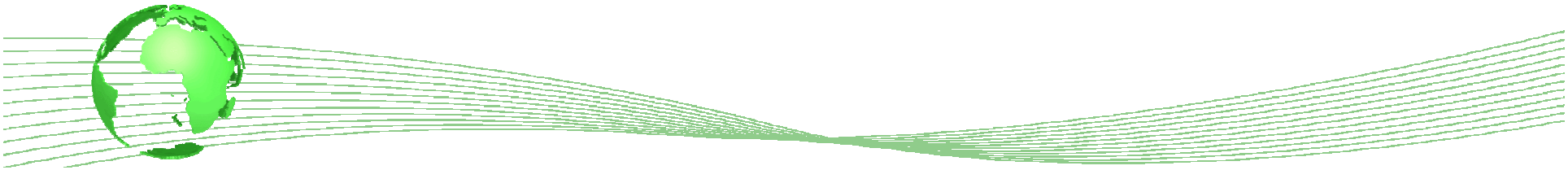
Zyme-Flow UN657 injected into a strategically chosen steam line over a 10 hour period

Continuous Monitoring

Throughout the 10 hour Vapour-Phase, gas concentrations were monitored until H_2S, LEL, and benzene all consistently read zero

Water Rinse with Zyme-Ox® Plus

Flushed any remaining scale, oxidized any additional pyrophorics, and cooled unit faster for manned entry



DECON TECHNOLOGY
ZYME FLOW®

Venezuela Coker Results

- Vessel was open and ready for inspection and hot work after 10 hours of Vapour-Phase
- Saved 7 days of mechanical preparation and cleaning
- All decontamination and maintenance work completed on schedule
- Tower free of oil with no traces of tarry hydrocarbon
- First time in vessel's history, the bottom manway was not obstructed by solids
- Easily swept out a single foot of fluff coke (hydrocarbon free)
- 84% reduction in effluent

Bottom distributor was accessible and completely unplugged

DECON TECHNOLOGY
ZYME FLOW®

Venezuela Coker Results

DECON TECHNOLOGY
ZYME FLOW®

Venezuela Coker Results

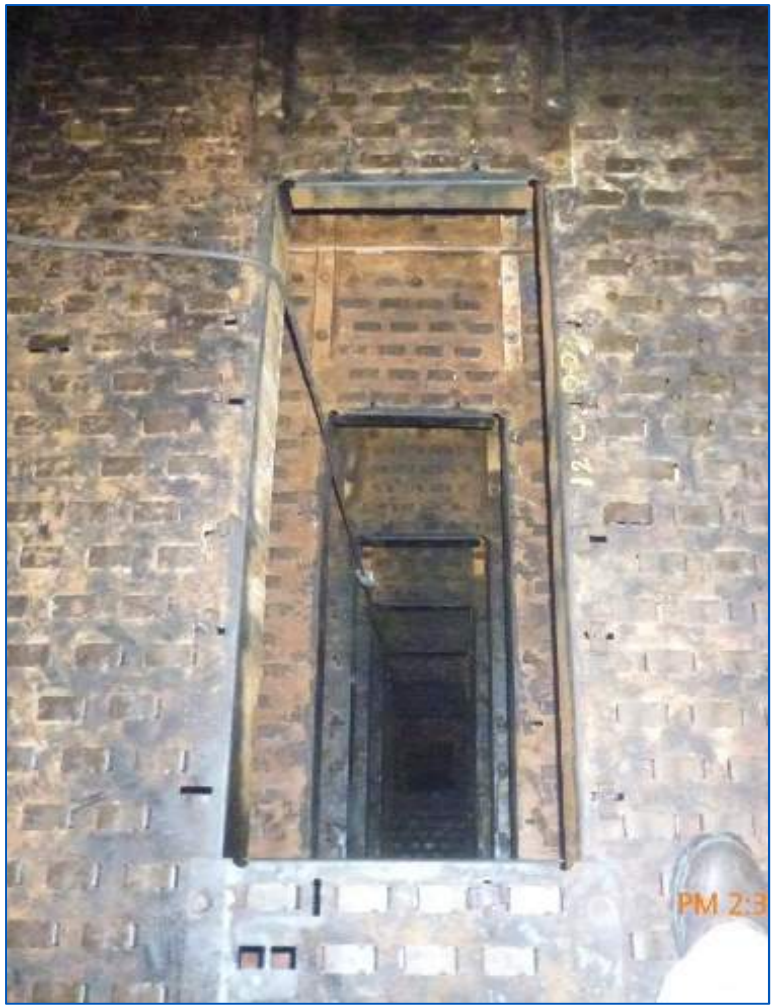
DECON TECHNOLOGY
ZYME FLOW®

Venezuela Coker Benefits

- Only 2 technicians per shift, 1 pneumatic pump, and 50 feet of half inch chemical hose
- Injection points connected to existing steam and process lines completed in less than one shift
- Eliminated several steps with simultaneous treatment of H_2S, LEL, and oxidation of pyrophorics
- 84% reduction in effluent; 6,875 gallons versus the 43,000 gallons with previous method

DECON TECHNOLOGY
ZYME FLOW®

Venezuela Coker Benefits



Effects on Effluent and Waste Generation

Background

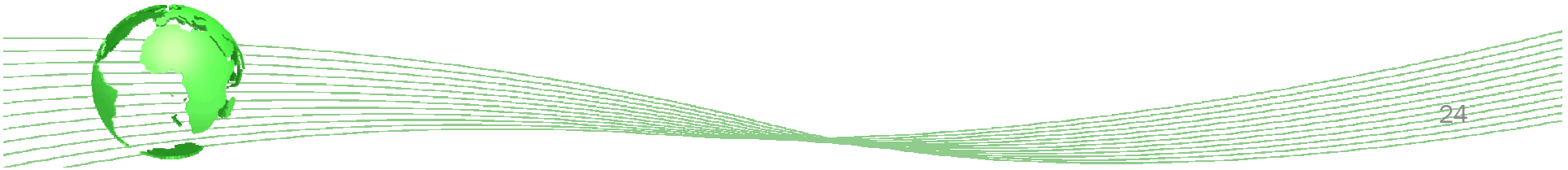
- No treatment facility on-site
- All effluent collected per site requirements

Oil Wash with Rezyd-HP

- Chemistry does not negatively effect cutter stock
- After circulation, cutter stock/chemistry combination sent to slop
- Only small dose required

ZymeFlow Vapour-Phase

- Large reduction in effluent (over 80% reduction) including post rinse
- Chemistry becomes part of steam – no water circulation required
- Reduced total steaming time (no pre or post steaming needed)
- Reduced cost; Non-hazardous



TCO Comparison – Venezuela Coker

	ZymeFlow Decon	Previous Chemical Contractor
Chemicals Utilized	3 chemistries	6 chemicals
Application and Hours	Vapour-Phase® 10 hrs	Circulation 36+ hrs
Mechanical Prep Time	<12 hrs	120 hrs
Personnel Required	2 techs per shift	12 man crew per shift
Equipment Setup	1 pneumatic pump, 50 feet ½ in. hose	Several chemical hose circuits, stage heated frac tanks, major mechanical, fork lifts
Special Requirements	None	Haz suites, secondary containment, barricades
Remaining Coke	<1' fluff coke	Tarry coke 2' above lower manway
Mechanical Cleaning	Fluff coke easily removed, no fresh air required	Extensive under fresh air
Effluent	6,875 gallons - no issues	43,000 gallons requiring disposal

DECON TECHNOLOGY
ZYME FLOW®

Conclusion

- Large differences between vessel entry methods – need to consider entire turnaround scope
- Methods are available that are faster and more efficient than mechanical-only removal of hardened deposits such as coke
- Decontamination affects not only on vessel entry but maintenance and entire turnaround schedule

DECON TECHNOLOGY
ZYME FLOW®

Worldwide Leader in Decontamination

- Decontamination specialists for over 25 years
- 200+ TAR and emergency outage projects/year
- Experience in over 50 countries
- Wide range of specialty blended chemistries
- Various application options including Vapour-Phase®
- Zero recordable injuries in 25 year history

Conclusion & Questions

www.ZymeFlow.com

Dr. Steve Matza
Chief Scientist
steve.matza@zymeflow.com