Catalyst management:

regeneration, reactivation, ex-situ sulfuration technologies

Gabriella Fogassy

20 March 2013, Sisak

Where we are located?

EURECAT IN THE WORLD

IFP Energies nouvelles — Axens (IFP Group Technologies)

ALBEMARLE®

EURECAT

Americas

Eurecat US
Pasadena/TX

Petroval US
Houston/TX

Tricat US
McAlester/OK

Europe

Eurecat France
La Voulte-sur-Rhône
Petroval SA
St Romain de Colbosc

Eco-Rigen
Gela, Italy

Tricat
Bitterfeld, Germany

Middle East

Al-Bilad Catalyst
Al-Jubail, Saudi Arabia

Asia

Eurecat India Catalyst Services
Jhagadia, Gujarat, India

Petroval AP
Eurecat Rep. Office
Singapore

STANDARDS & VALUES

Responsible Care Program

Quality ISO 9001 certification

Environmental ISO 14001 certification

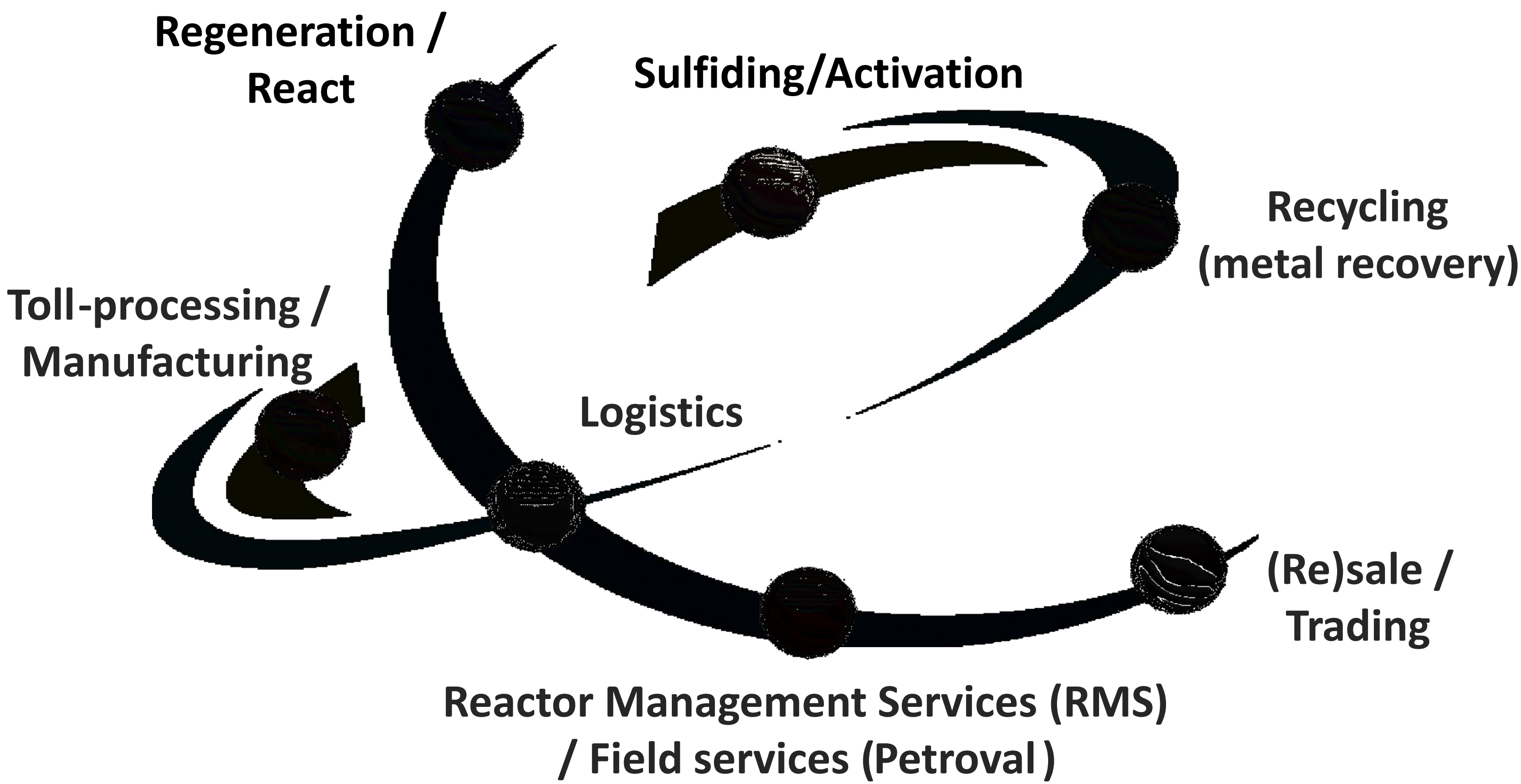
Safety OHSAS* 18001 certification or equivalent

*(*Occupational Health and Safety Assessment Series)*

Our values:

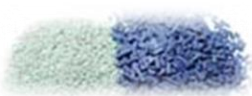
- Innovation
- Customer satisfaction
- Confidentiality
- Ethics

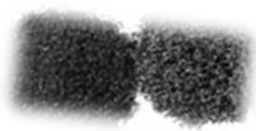
SERVICES, PRODUCTS & TREATMENT



UNIT OPERATION/CATALYST LIFE CYCLE

Metal reclaim





Fresh → Loading → Startup → Run → Unloading → Regeneration Reactivation

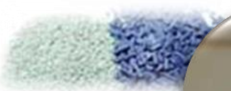
Startup: In-situ sulfiding

Run: Activity Δp

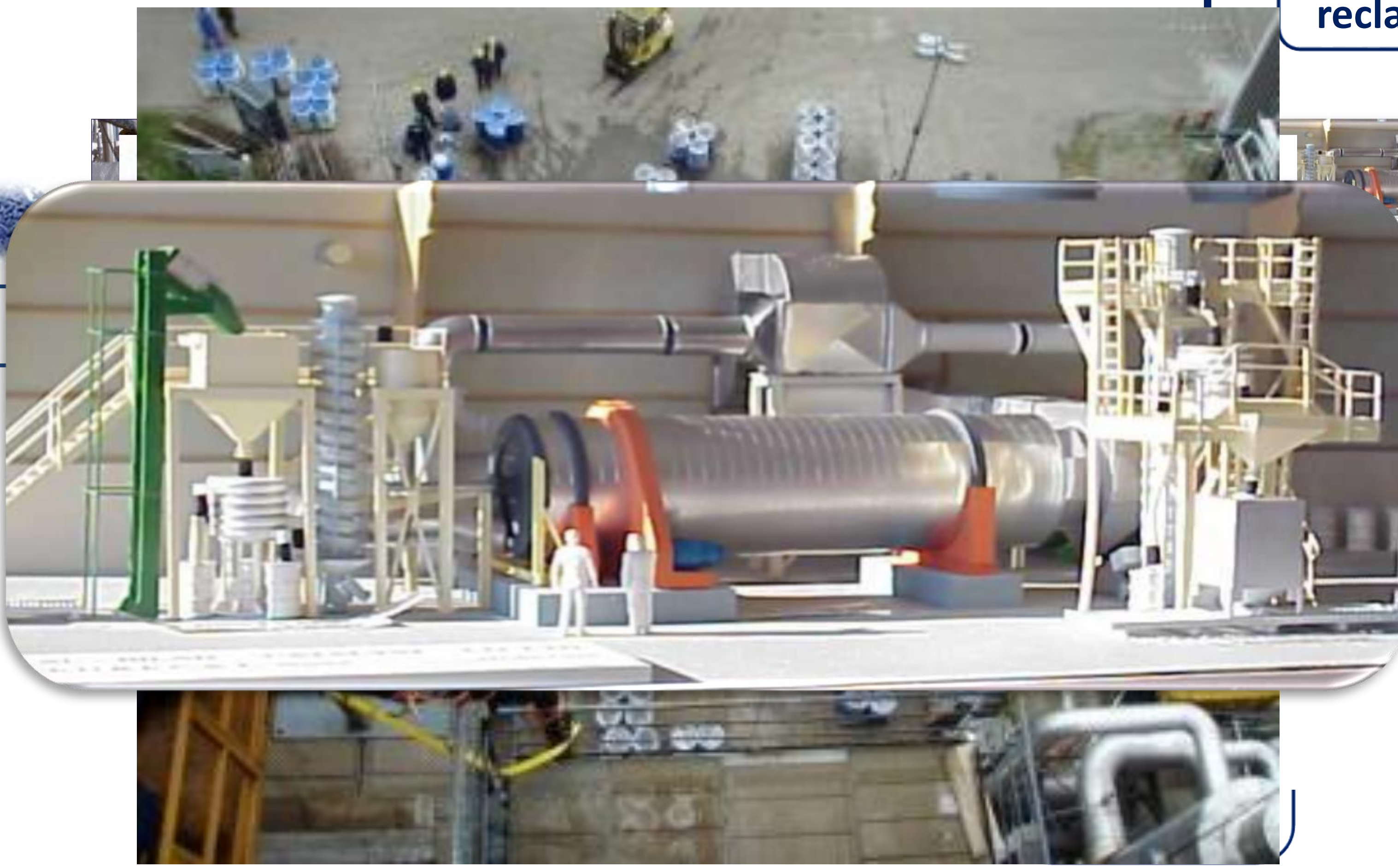
REUSE
CASCADING
POOL
RESALE

UNIT OPERATION/CATALYST LIFE CYCLE

Metal reclaim



Fresh



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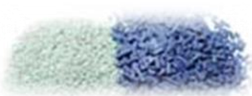
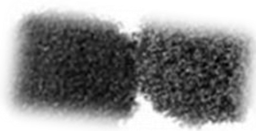
UNIT OPERATION/CATALYST LIFE CYCLE





Fresh → Loading → Startup → Run → Unloading → Regeneration Reactivation

Startup: In-situ sulfiding

Run: Activity Δp

Unloading: SMARTDUMP CARBODUMP

Unloading → Metal reclaim

Regeneration Reactivation → REUSE CASCADING POOL RESALE → Initial activity Δp prediction → Ex-situ Sulfiding: TOTSUCAT → Loading

UNIT OPERATION/CATALYST LIFE CYCLE

Fres[redacted]

tion
ion

REGENERATION TECHNOLOGIES

CONVENTIONAL REGENERATION

- Zeolites
- Ni Catalysts
- Pd Catalysts
- CoMo, NiMo, NiW Catalysts

DRY REGENERATION

- Zeolites (Confidential)

REJUVENATION

- CoMo, NiMo catalysts

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Deactivation mechanisms of HPC

2. **Structural modifications:**
   – Sintering of metallic particles
   – Migrations and/or losses of active species
   – Structure changes

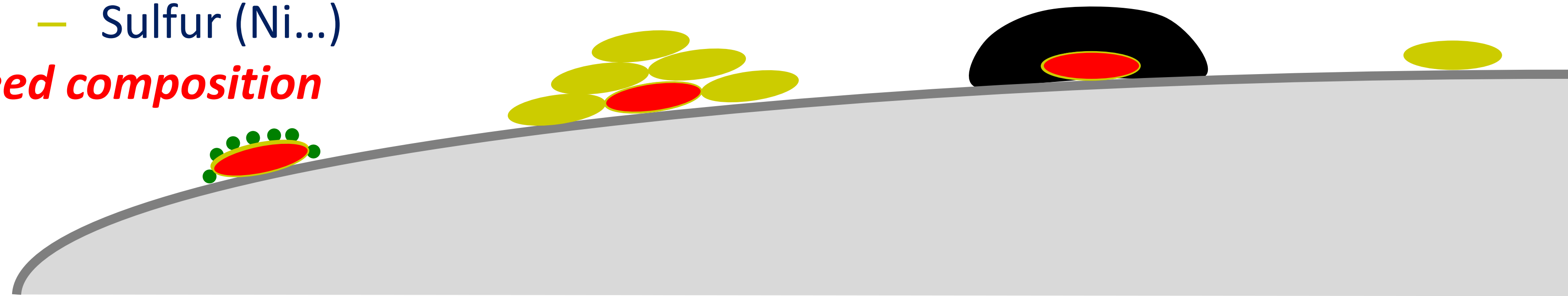
   Function of operating conditions

3. **Irreversible poisoning:**
   – Metallic contaminants (V, Fe, As, Hg…)
   – Silicon, sodium…
   – Sulfur (Ni…)

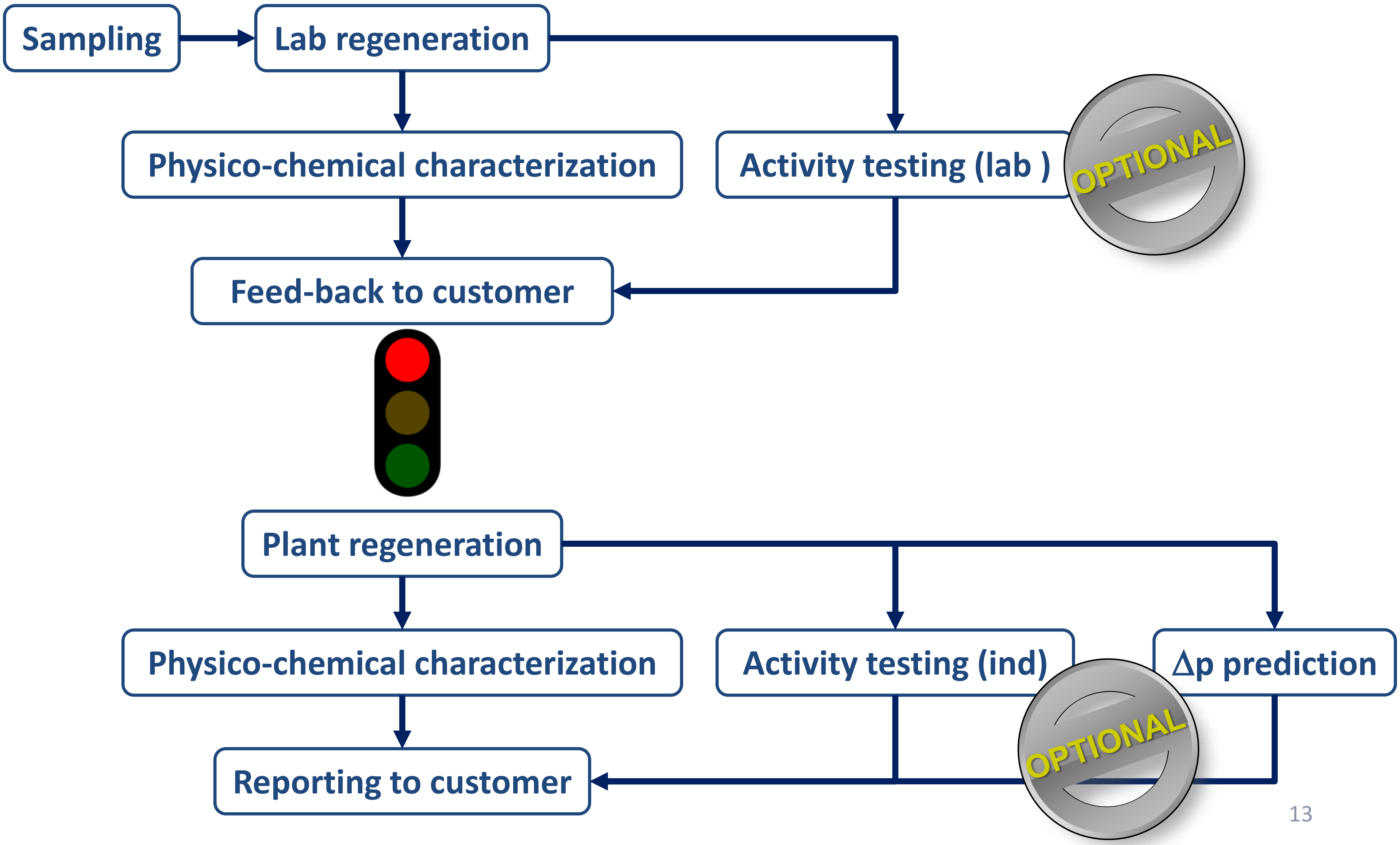
Feed composition

1. **Reversible poisoning:**
   – Carbon: 5-25%
   – Basic nitrogen (Hydrocracking)

   From side reactions



HPC TREATMENT



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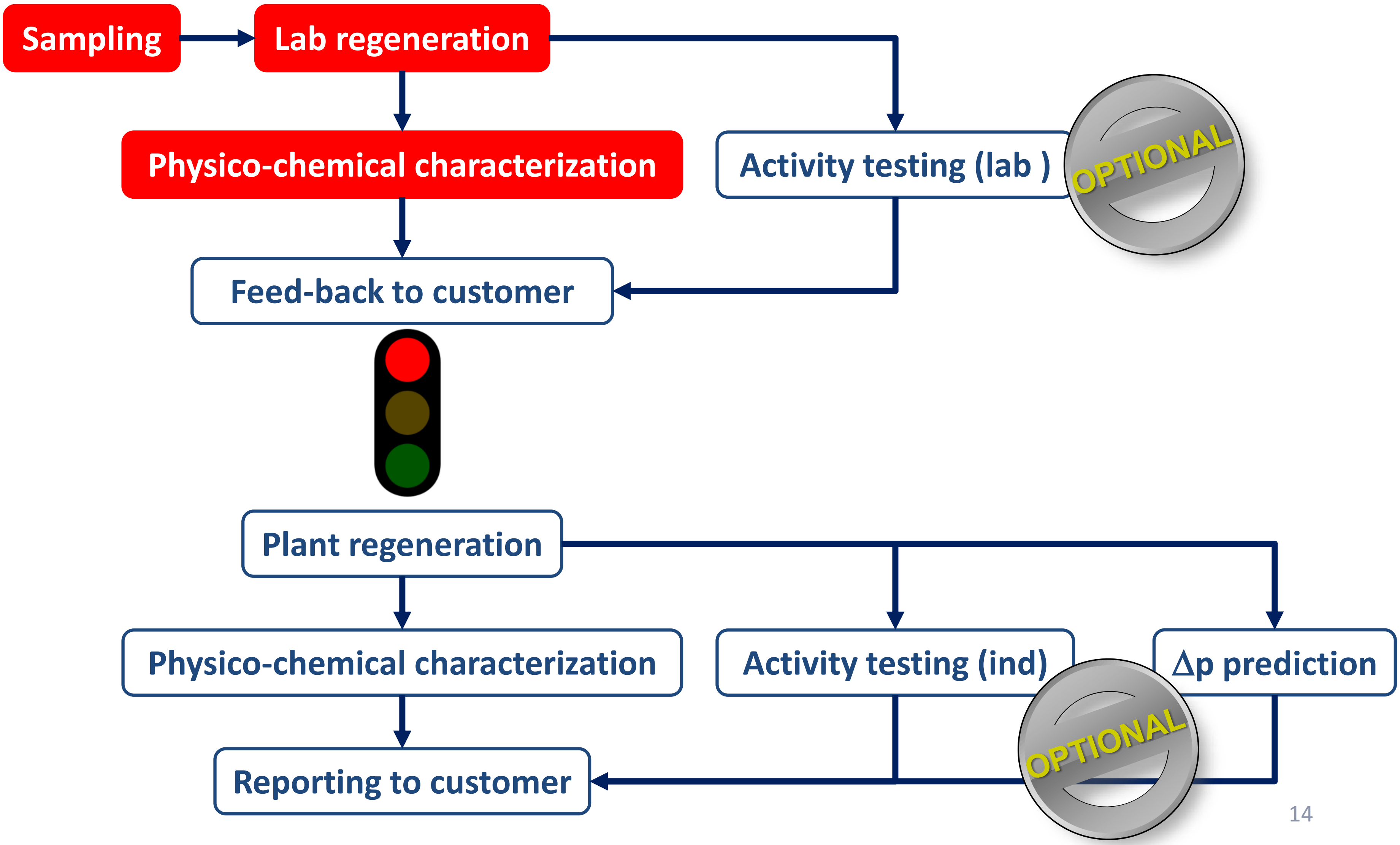


Sampling/Analysis

1 representative sample of the bed

Standard

sampling procedure

(for each bed)

15-30 samples are taken and

mixed together and

homogenized before

characterization

Bed profile

Dedicated SAS

sampling procedure

(for each bed)

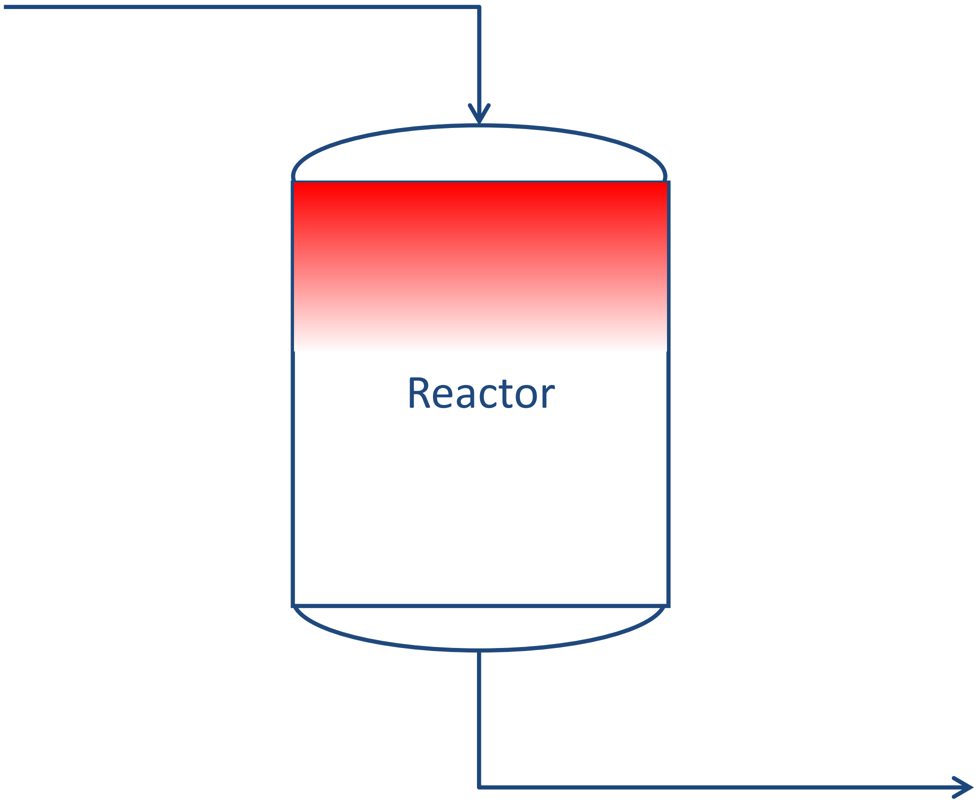
15-30 samples are taken and

all samples are kept separated

for individual characterization

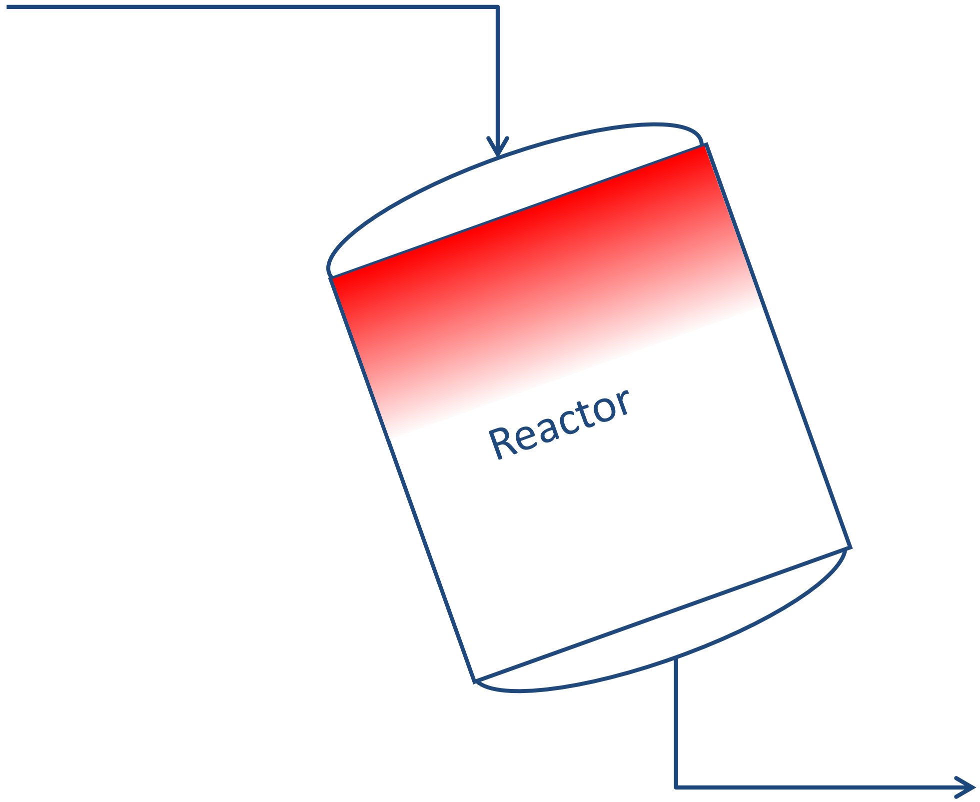
OPTIONAL

MAXIMISE RECOVERY SAS (SAMPLE/ANALYSE/SEGREGATE)



Catalyst is often partly contaminated, partly in good shape

SAS: SAMPLE/ANALYSE/SEGREGATE



Catalyst is often partly contaminated, partly in good shape

- **Allows to trace metals contamination vs height in reactor.**

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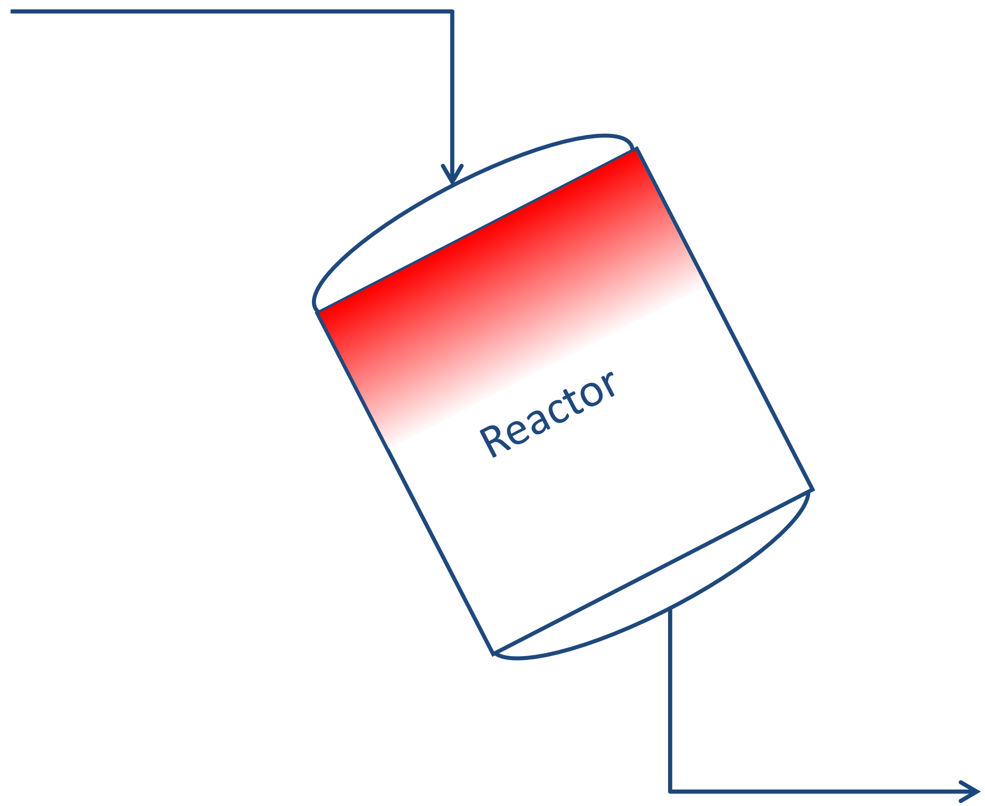

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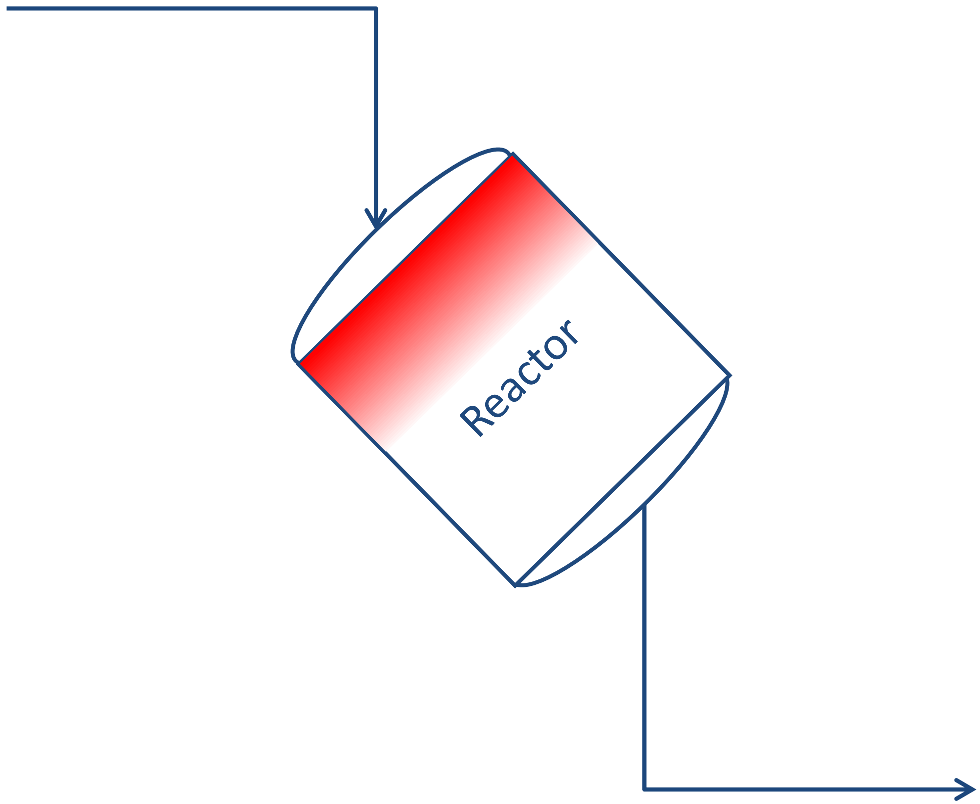

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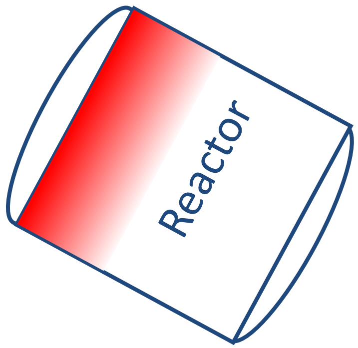

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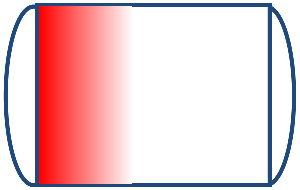

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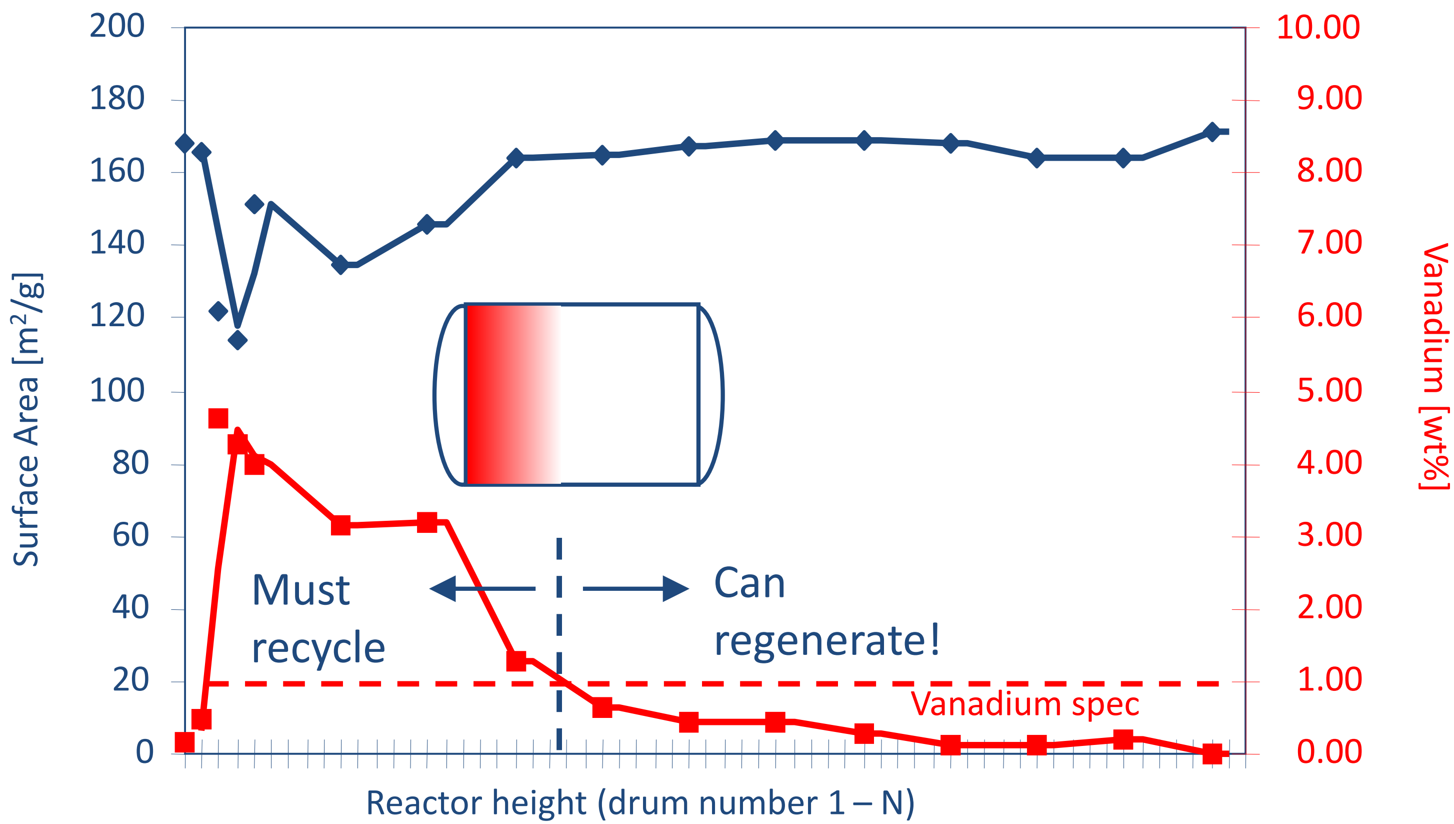
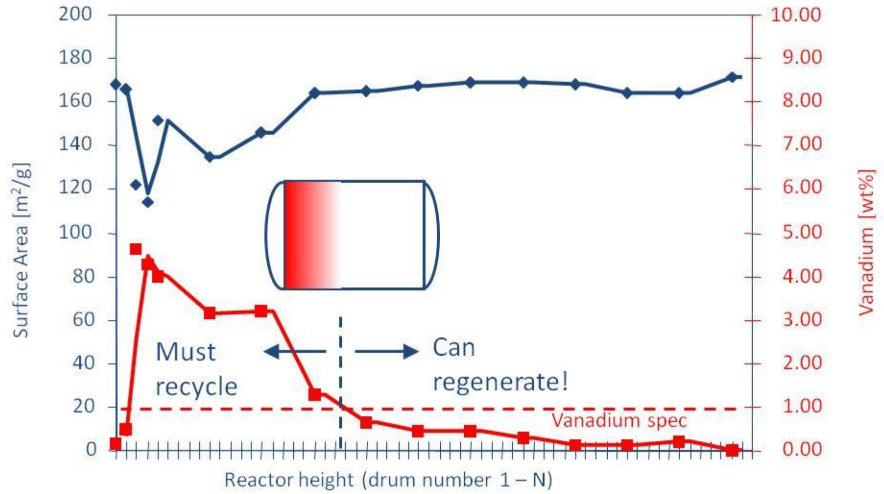


- ❑ **Drums/bins should be numbered during unloading!!!**
- ❑ **Allows to trace metals contamination vs height in reactor.**

SAS: SAMPLE/ANALYSE/SEGREGATE



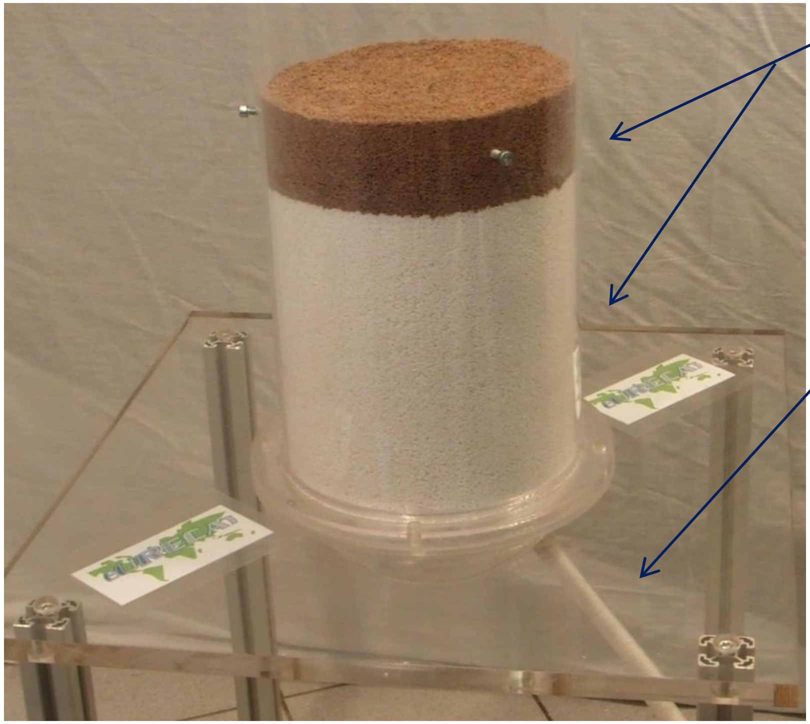
Case study of 96 tons reactor

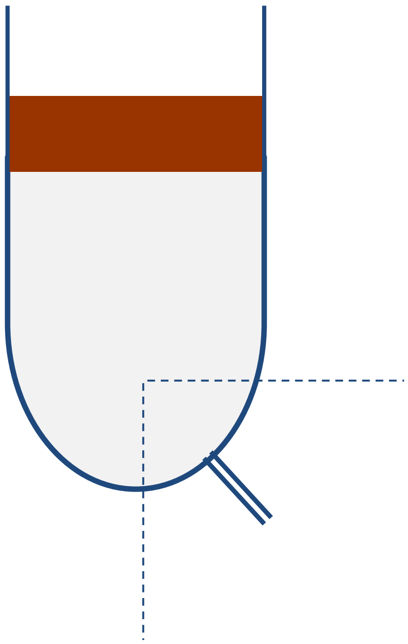
- Average analyses slightly off-spec
- Refiner wanted to send batch for metals recovery.
- SAS pointed out contamination was very local
- 75% of catalyst could be recovered
- 1.3 M$ savings

FROM GRAVITY DUMPING TO SAS

2 stacked beds – dense load

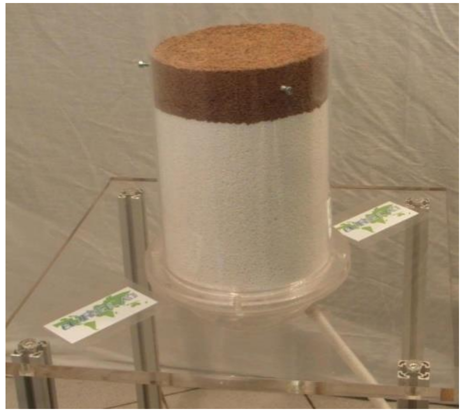
1 dump pipe (45°)





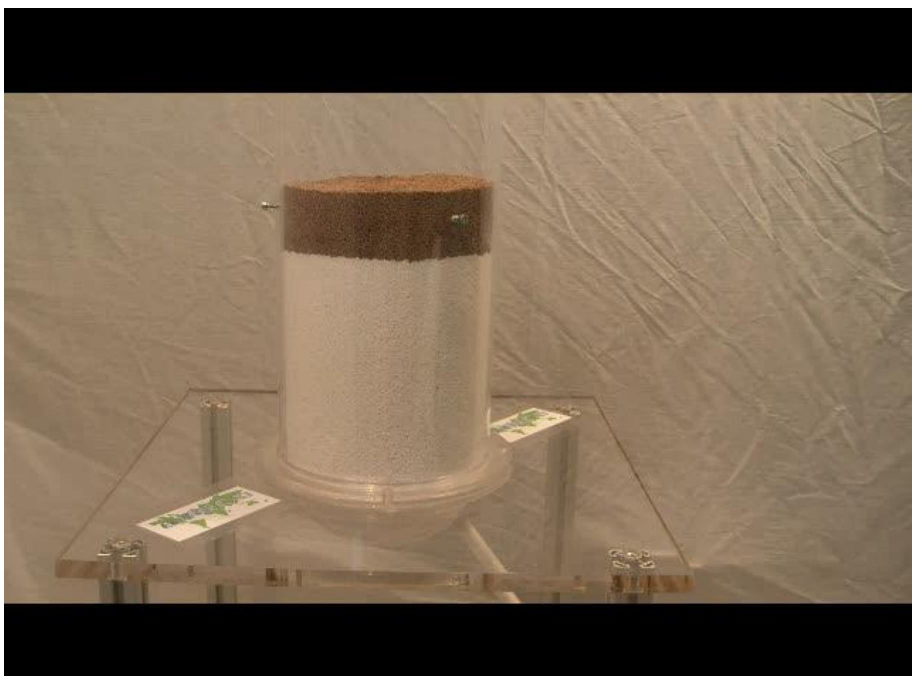
Diameter = 24 cm
Height = 1 m

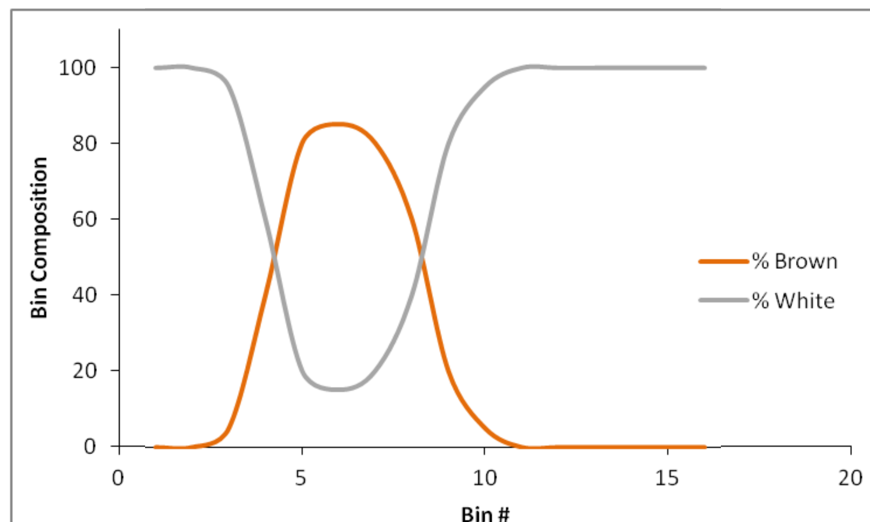
From Gravity dumping



Side view

Front view

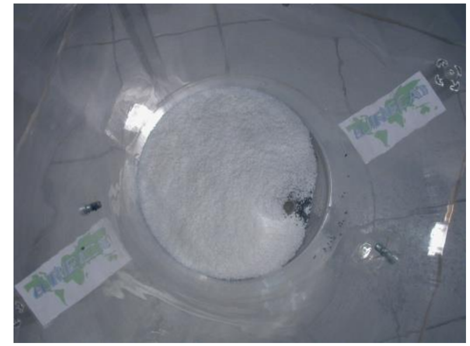




TO SAS

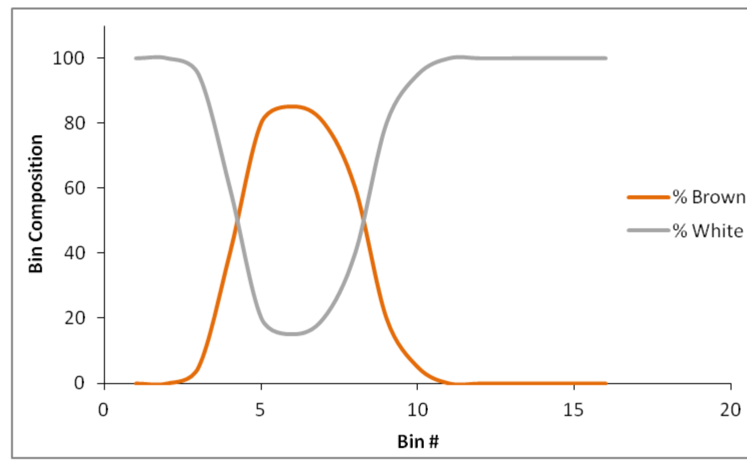
Dig out

Conical shape



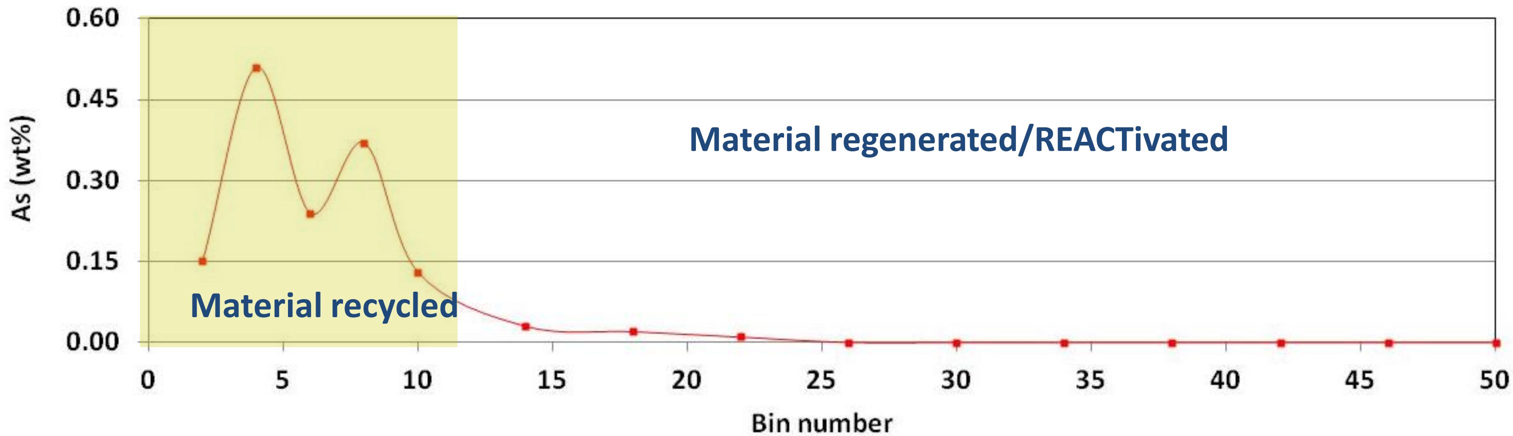
SAS

Gravity Unloading



- After Gravity dump, SAS can trace back the position of the catalyst in the reactor.

TO SAS



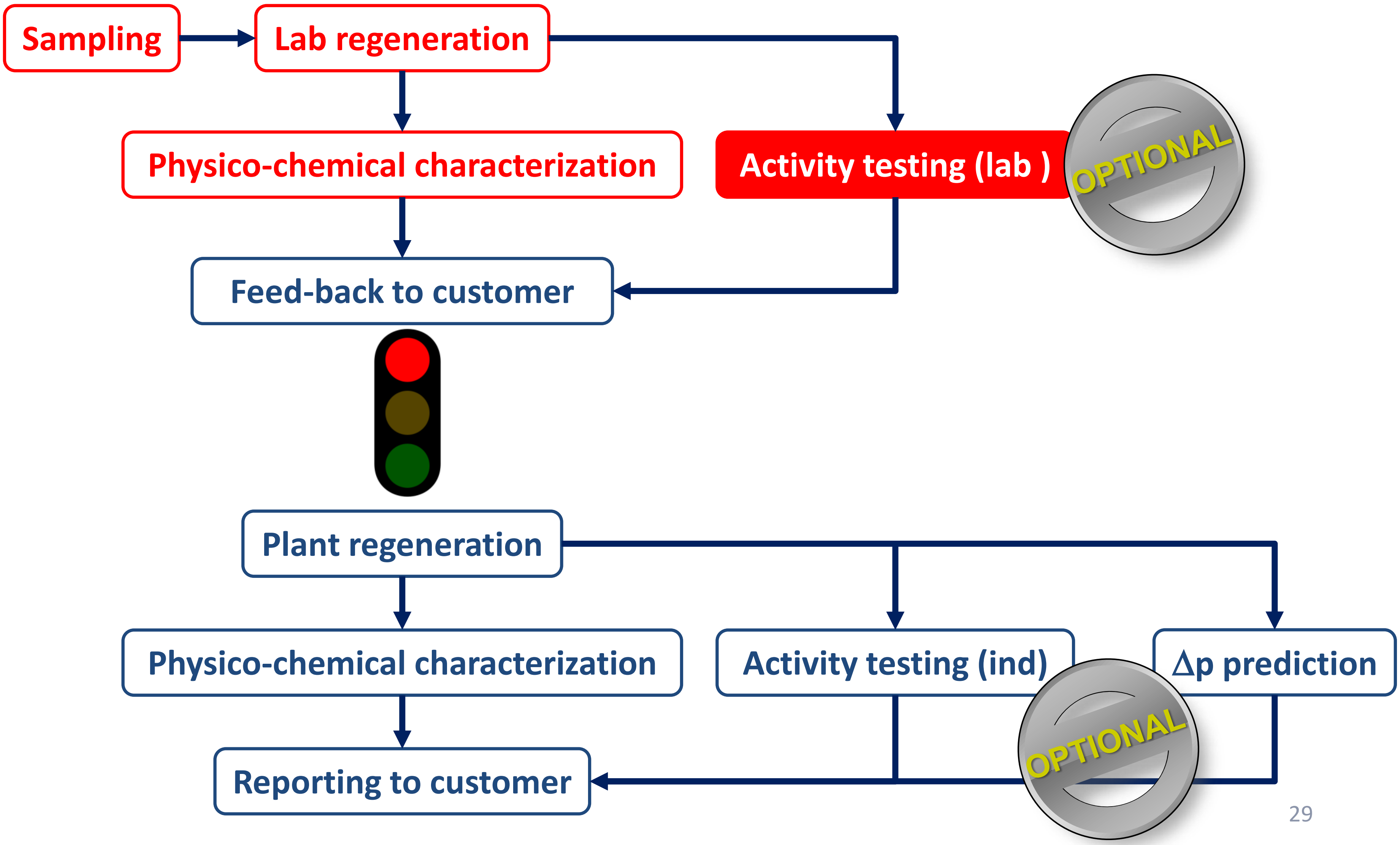
N° BINS	As (wt%)	V (wt%)	Fe (wt%)	Si (wt%)	Na (wt%)	C spent (wt%)	S spent (wt%)	C lab reg (wt%)	S lab reg (wt%)	SA (m^2/g)	Lmm (mm)	%grains < 1.5mm	%grains < 2.0mm
2	0.15	0.00	0.12	0.15	0.09	10.8	13.6	0.1	0.6	141	2.67	6	22
4	0.51	0.00	0.13	0.17	0.07								
6	0.24	0.00	0.13	0.17	0.11	9.5	14.3	0.1	0.8	143	3	4	18
8	0.37	0.00	0.14	0.17	0.14								
10	0.13	0.00	0.11	0.15	0.08	9.1	13.9	0.1	0.6	142	3.04	2	10
14	0.03	0.00	0.10	0.15	0.08	9.5	13.5	0.1	0.6	142			
18	0.02	0.00	0.08	0.16	0.06	10.2	14.2	0.1	0.4	151	2.84	4	15
22	0.01	0.00	0.08	0.15	0.08	10.9	14.1	0.1	0.3	154			
26	0.00	0.00	0.07	0.14	0.05	11.0	13.7	0.1	0.4	160	3.31	3	9
30	0.00	0.00	0.06	0.15	0.05	11.0	13.8	0.1	0.3	162			
34	0.00	0.00	0.06	0.14	0.04	10.3	14.0	0.1	0.3	152	2.85	4	15
38	0.00	0.00	0.07	0.15	0.05	11.4	14.1	0.1	0.3	162			
42	0.00	0.00	0.06	0.16	0.05	12.0	13.4	0.1	0.2	158	3.00	5	14
46	0.00	0.00	0.06	0.15	0.04	12.0	14.0	0.1	0.3	153			
50	0.00	0.00	0.06	0.15	0.05	12.0	13.7	0.1	0.3	160	2.66	10	26
Average	0.10	0.00	0.09	0.15	0.07	10.7	13.9	0.1	0.4	152	2.89	5	16

LAB REGENERATED CATALYST ANALYSIS

Lab regenerated HPC catalyst

- Carbon
- Sulfur
- Surface area
- BCS (Bulk Crushing Strength) and/or SCS (Side Crushing Strength)
- Abrasion loss
- Average length
- PSD (Particle Size Distribution)
- Poisons (As, V, Fe, Si, Na, Ni,…)

HPC TREATMENT

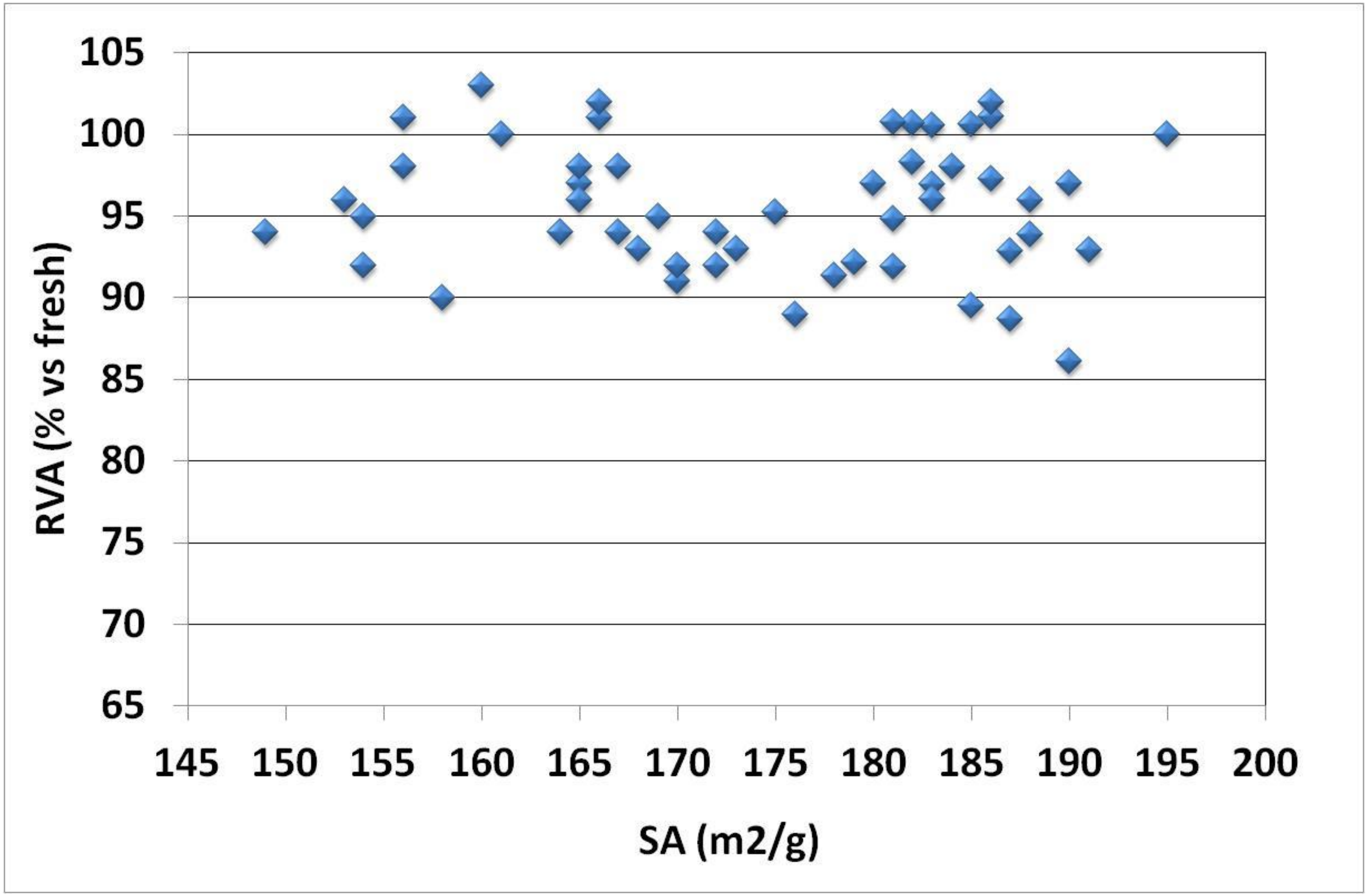


- Activity recovery is highly dependent on spent catalyst condition.
- Catalyst activity cannot be well quantified from analytical properties.

Direct activity testing is indispensable to assess reusability.

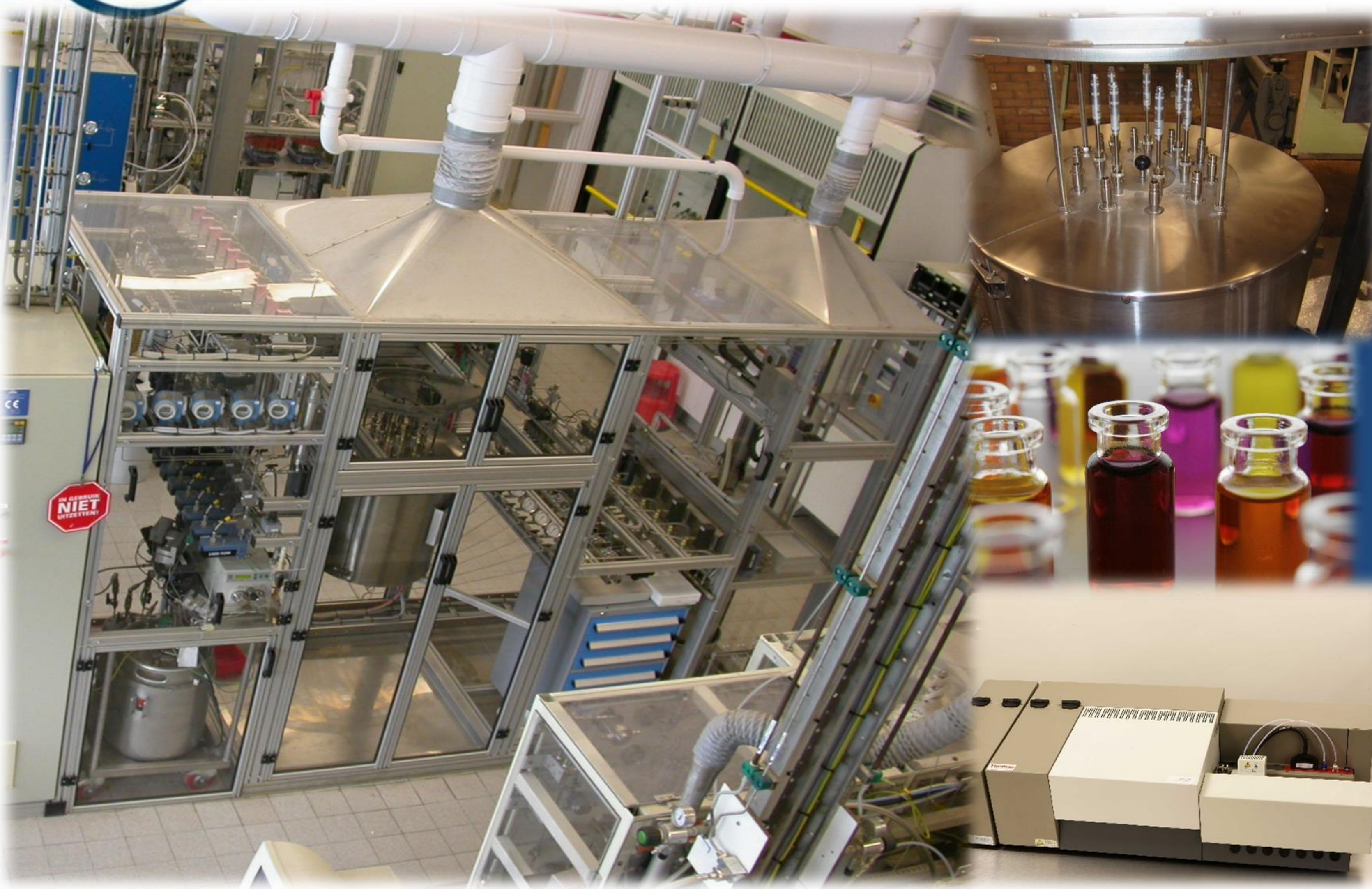
RVA / RWA (%) measured correlates directly to reactor WABT (°C).

ACTIVITY VS SURFACE AREA KF757



No relevant metals contamination on every batch

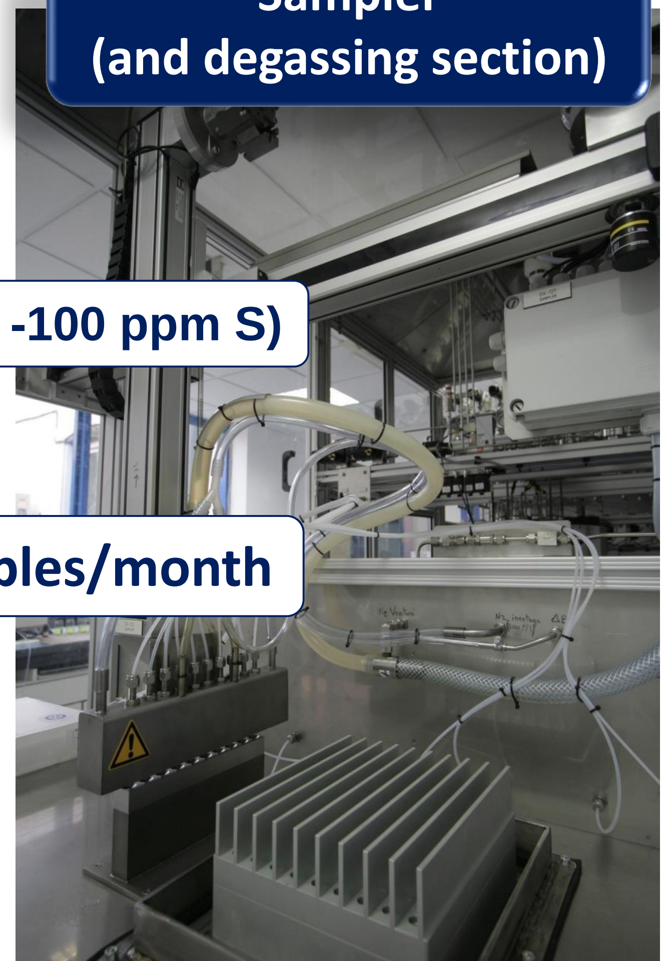
ACTIVITY TEST



MTU OVERWIEV

Furnace and 10 reactors in parallel

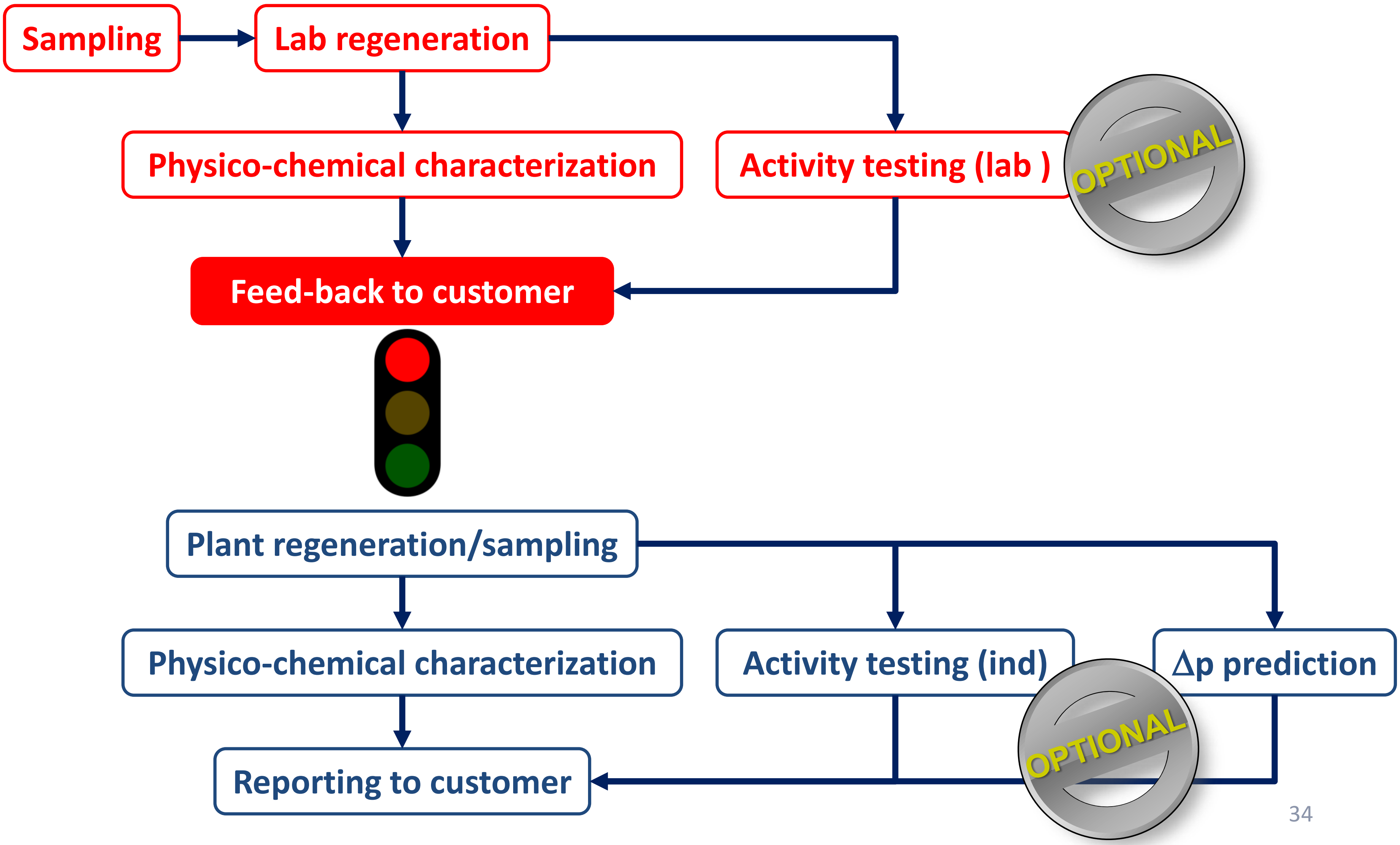
Sampler (and degassing section)



HDS – ULSD (10 -100 ppm S)

Capacity: 80 samples/month

HPC TREATMENT



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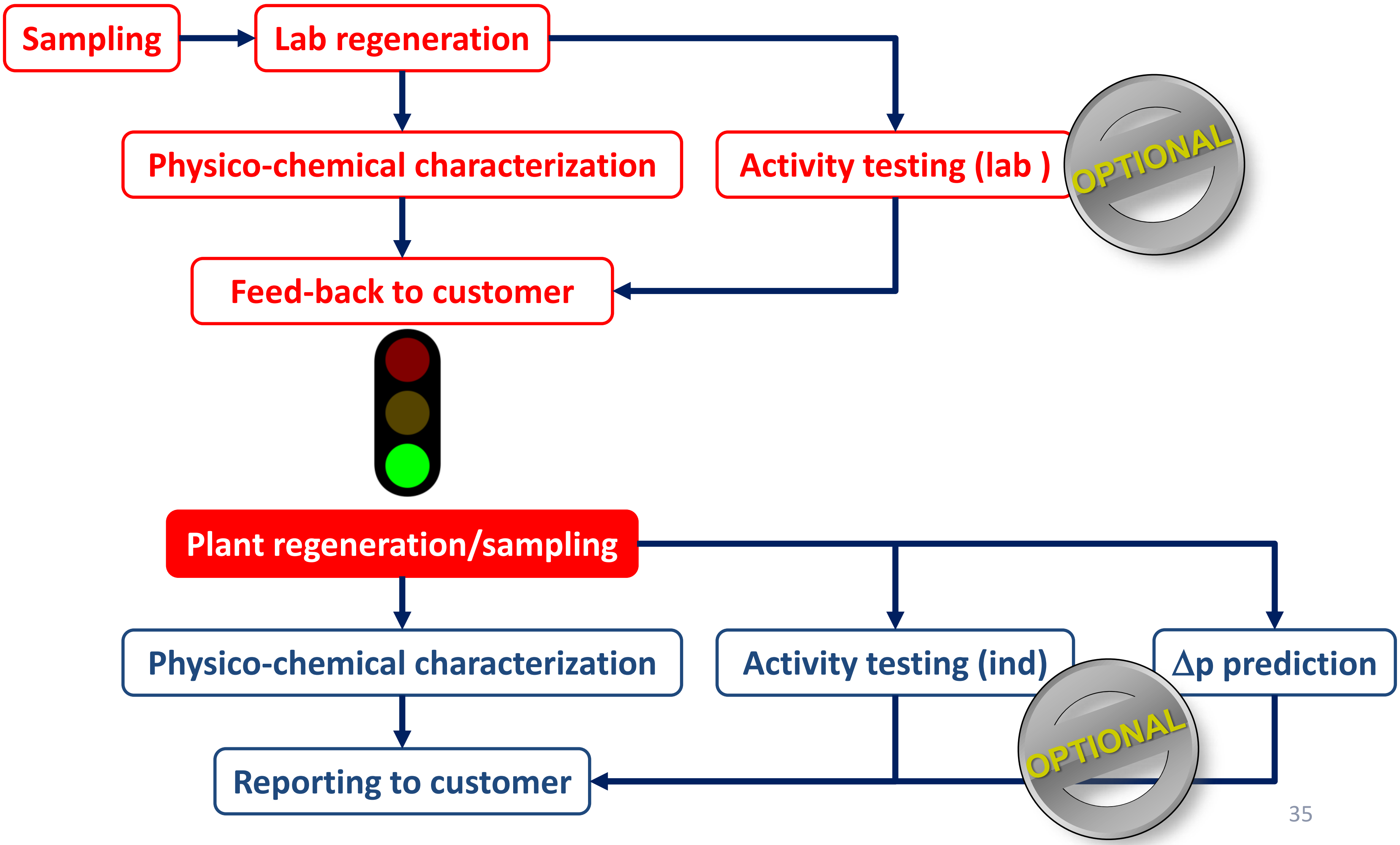
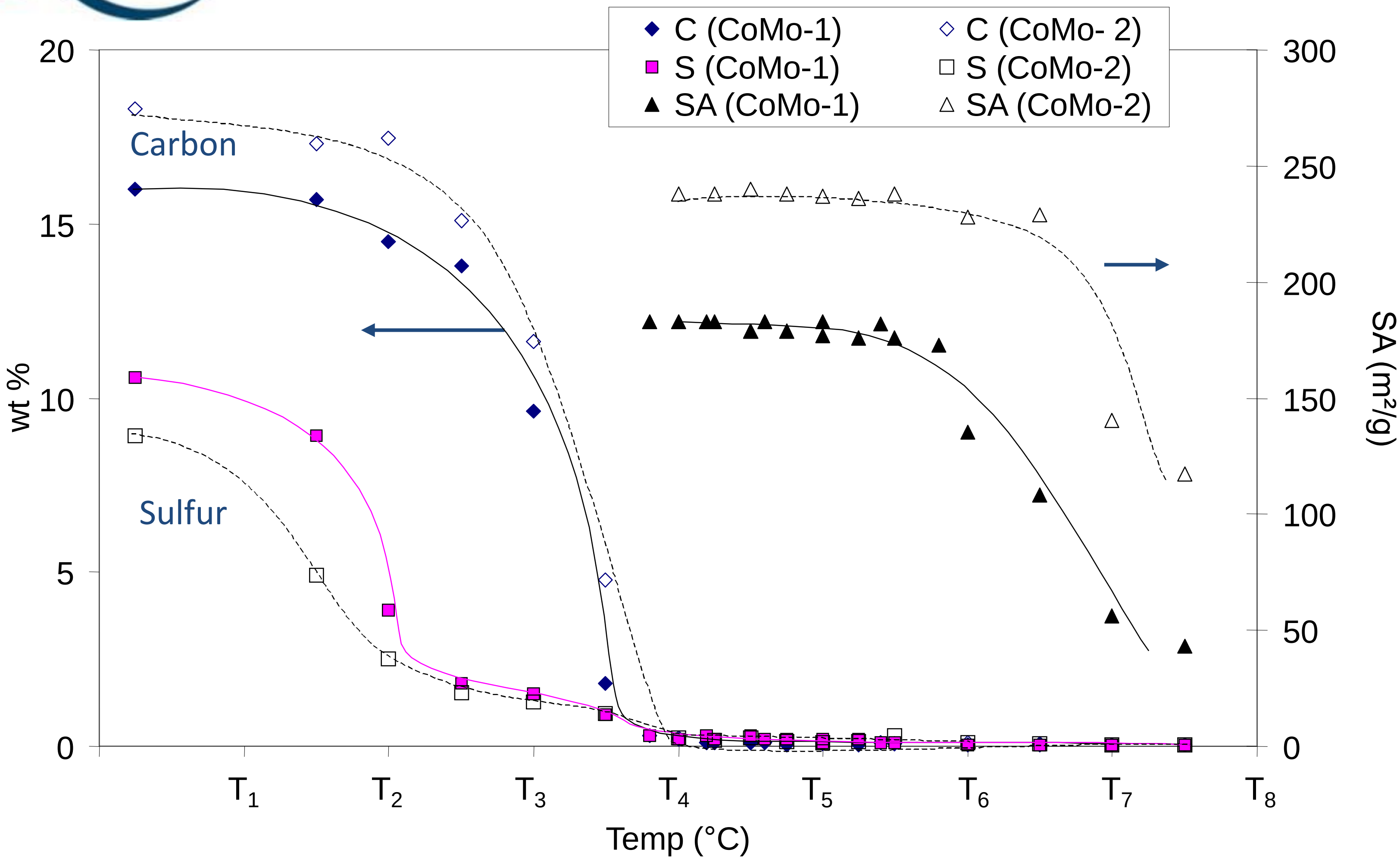


REGENERATION PARAMETERS OF HPC

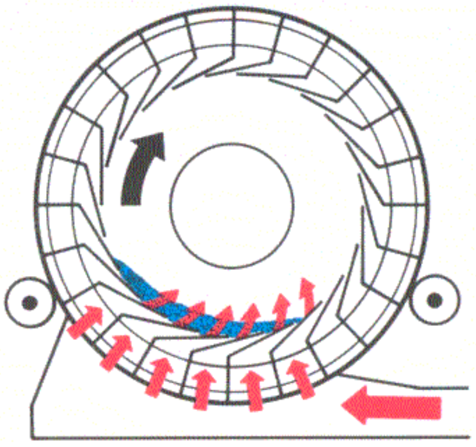


2 Commercial Hydrotreating catalyst - CoMo on Al_2O_3

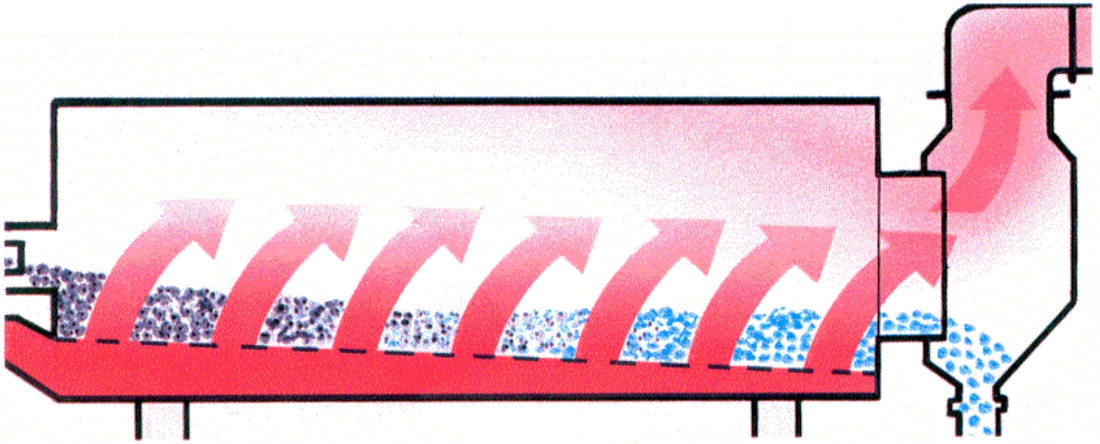
Tailor-made recipes for each individual catalyst

Maximum activity recovery:

- homogeneous regeneration
- strict temperature control
- rapid heat and H_2O/SO_2 removal

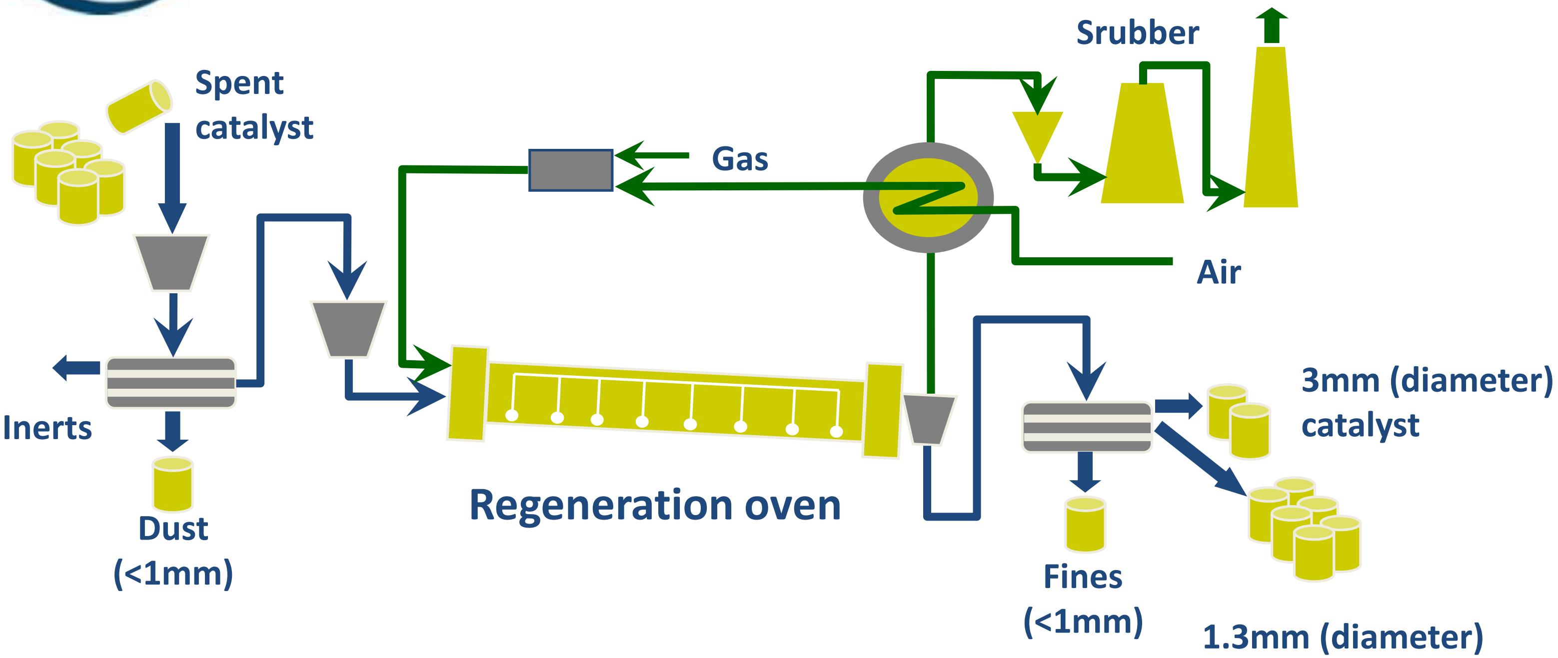


Cross view



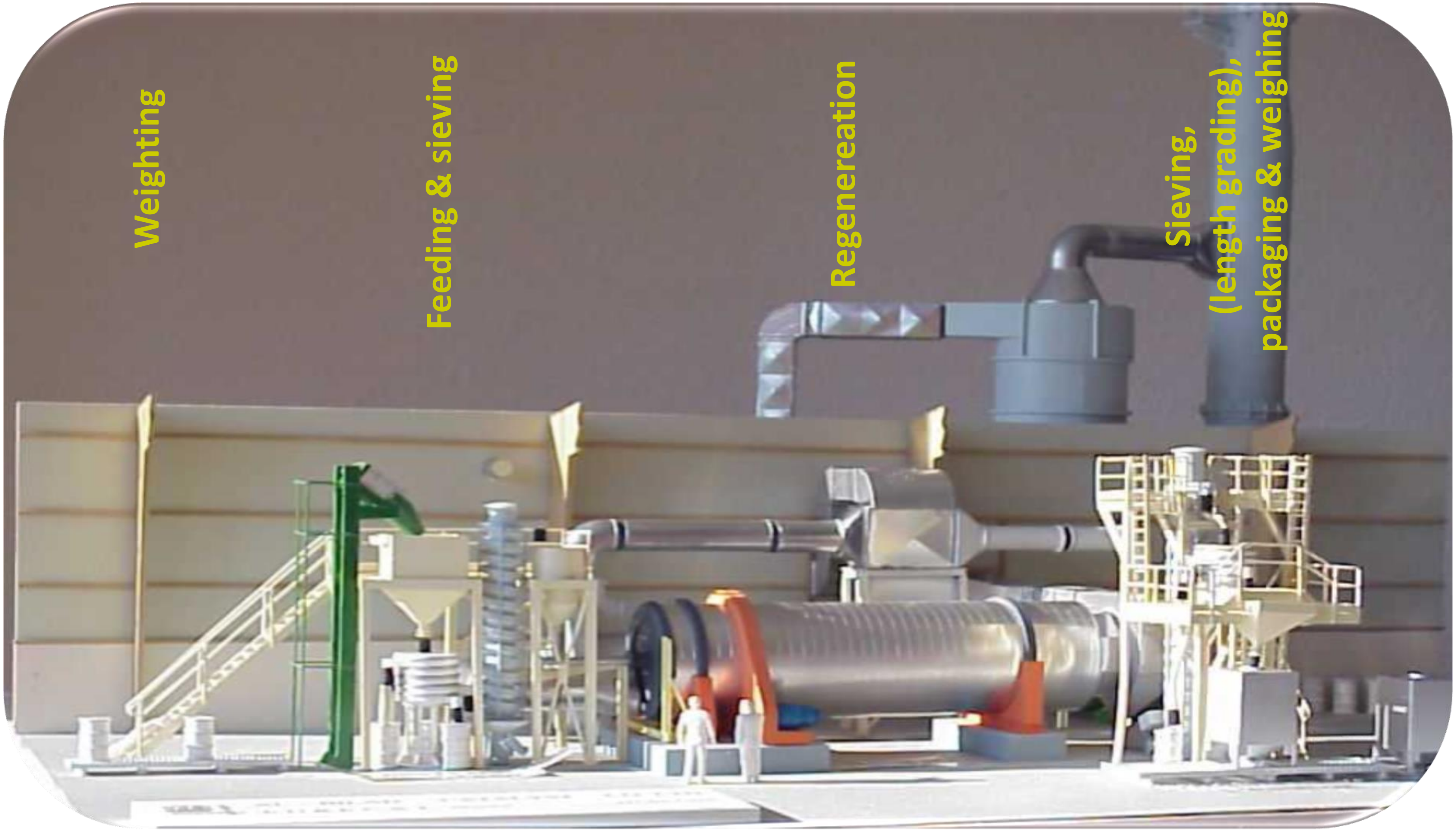
Side view

REGNERATION FLOW SHEET



- ❑ Continuous process
- ❑ High activity recovery (≥ 95 % SA retention)
- ❑ Fines guaranteed to be less than 1 wt%
- ❑ Fine-tuned to each different catalyst
- ❑ Catalyst evaluation (QC)

PLANT REGENERATION



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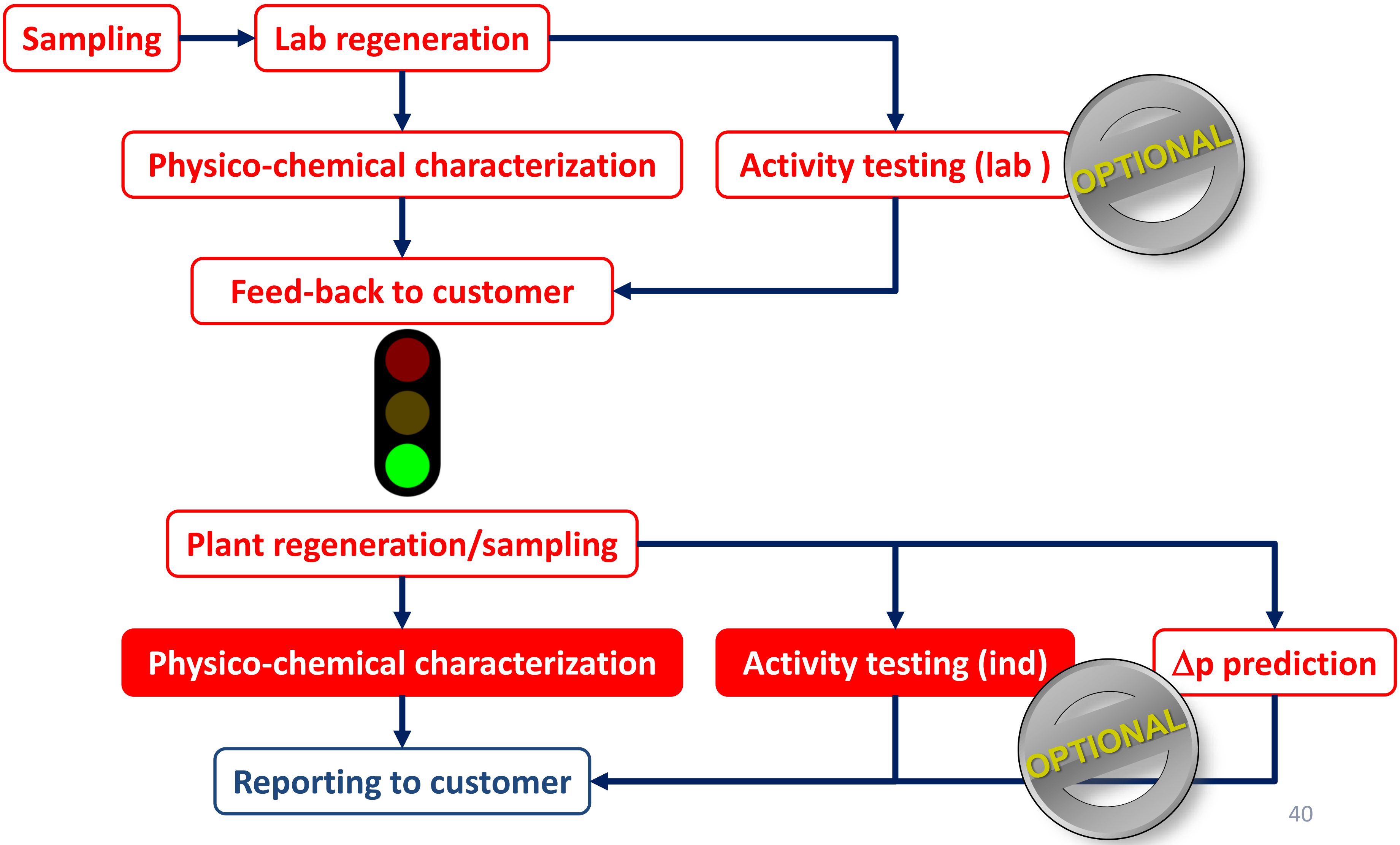

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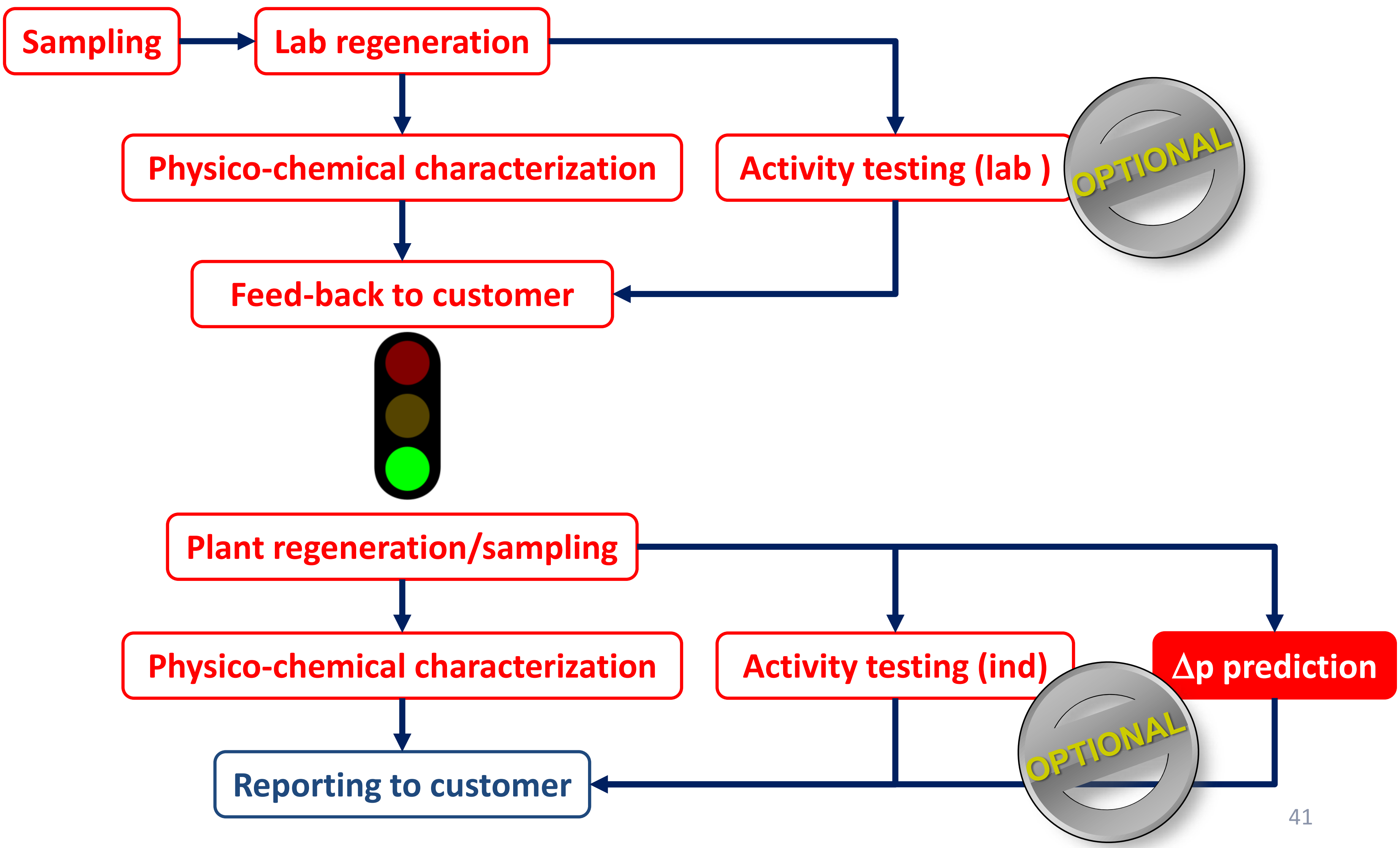


Catalyst Performance: Pressure drop

- Eurecat has developed unique pressure drop measurement to predict mixed phase delta P in refinery reactor conditions.

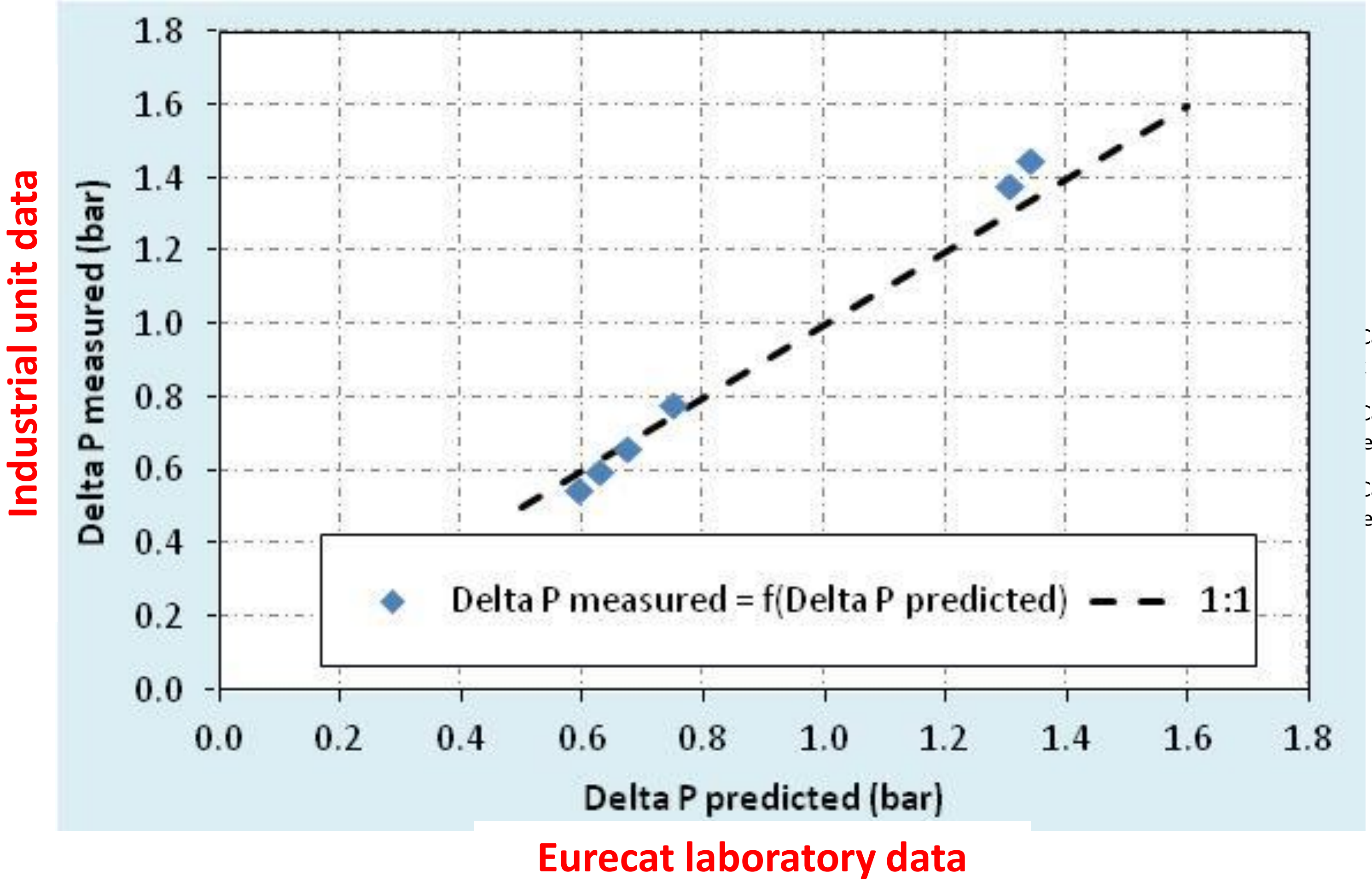
Eurecat
Lab gas phase ΔPref measurement
+ Lab gas phase ΔP measurement
+ Correlation

Commercial
ΔPref (bar)

Predicted ΔP
(bar)

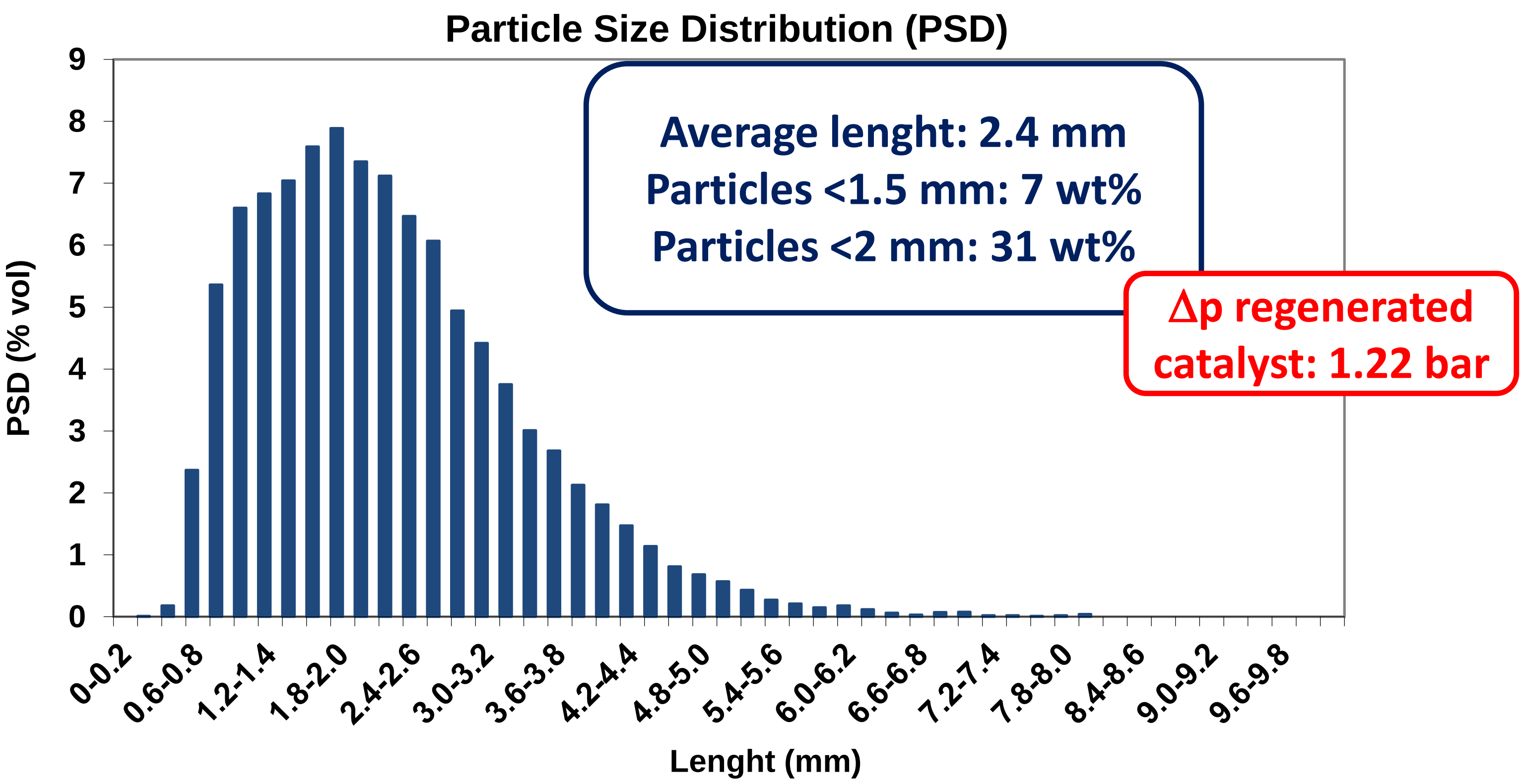
Catalyst Performance: Pressure drop

- Tool has been validated in refinery units (multibed, dense/sock):

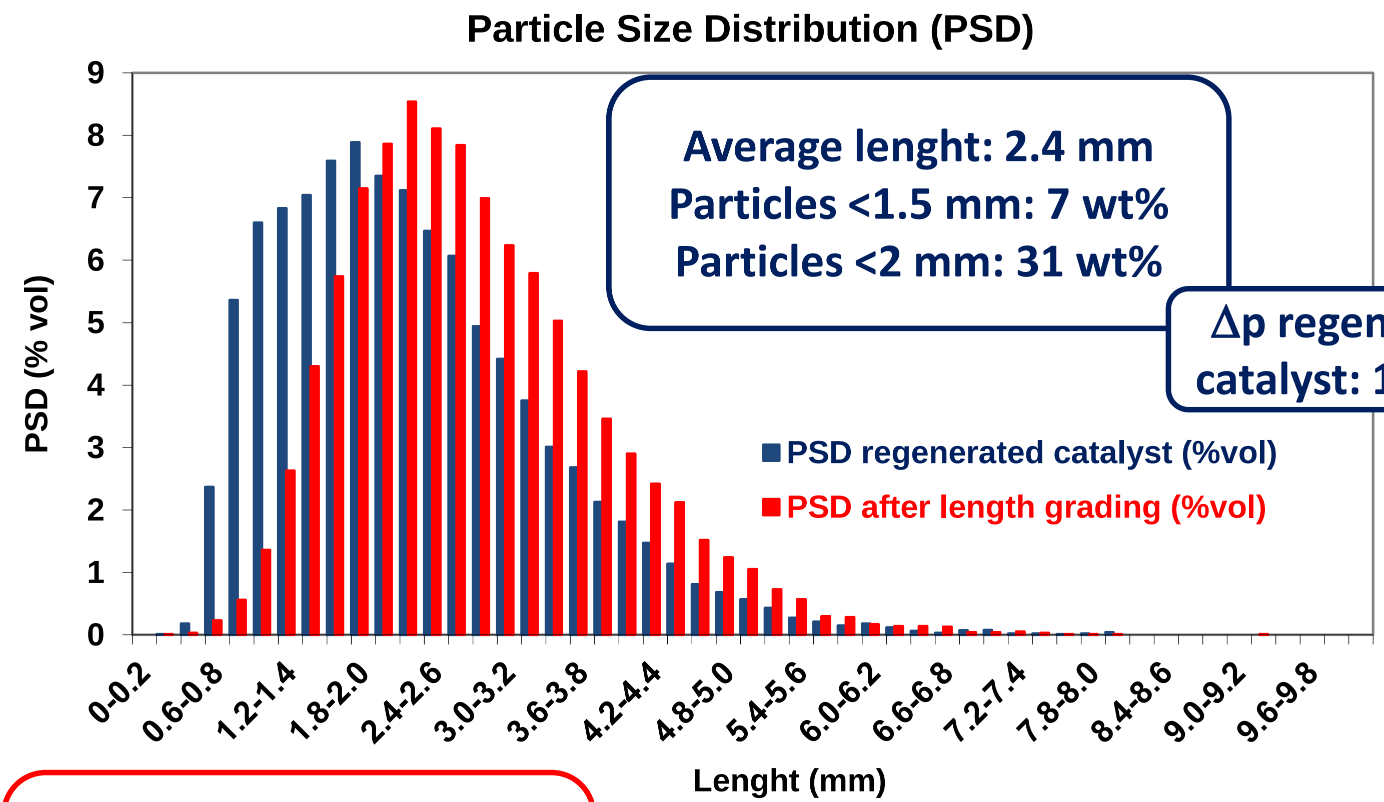


Cat 3
loading
Cat 4
e loading
Cat 4
e loading

PARTICULE SIZE DISTRIBUTION VS PRESSURE DROP



LENGTH GRADING VS PRESSURE DROP



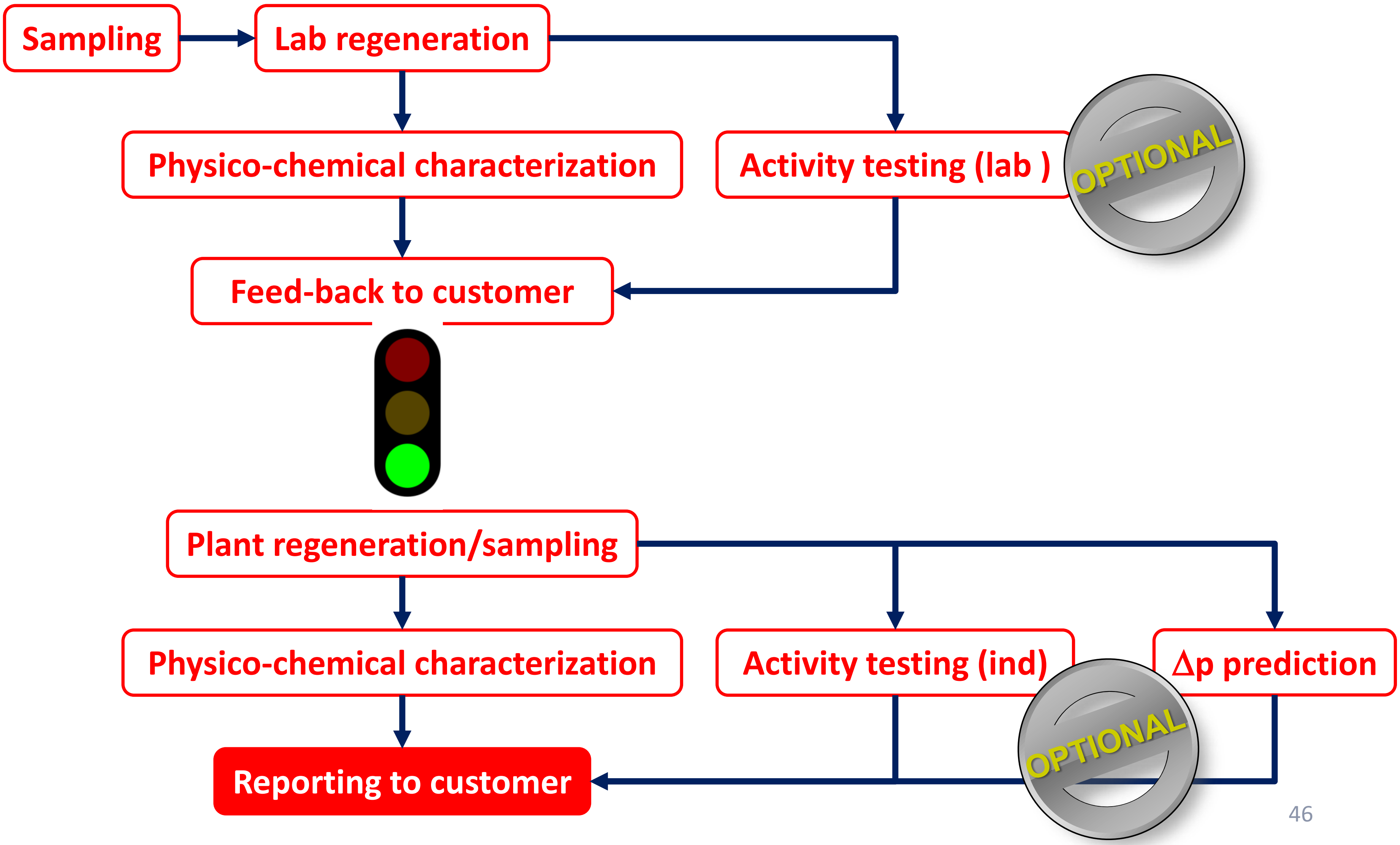
Average lenght: 2.4 mm
Particles <1.5 mm: 7 wt%
Particles <2 mm: 31 wt%

Δp regenerated catalyst: 1.22 bar

Average lenght: 2.9 mm
Particles <1.5 mm: 2 wt%
Particles <2 mm: 15 wt%

Δp after lenght grading: 1.01 bar

HPC TREATMENT



Regeneration report

1XXXX/A KF757 3Q

Comments:
FB 66-68 : 40 wt % dust

PO number:
End of treatment: 31/1/2013

Mass balance

Inerts: (kg) 3528 16 drum(s)

Unregenerated material:
net: (kg)
57983 68 bins

Initial screening → 53201 → REGENERATION → Final screening

Regenerated catalyst: **net: (kg)**

KF757\3Q	**998**	1 BB
KF767 1.5E	**42100**	43 BB

Dust: (kg) 1254 7 drum(s)

Fines: (kg) 368 11 drum(s)

Catalyst characteristic

		[illegible]ab regen:	Spec:	Regen:	Notes:
LOI (wt%):	18.3	-	-	-	
Smoke test:	Yes	-	-	-	
HC/other volatiles (wt%)	2.9	-	-	-	
C (wt%):	14.2	0.1	0.5	0.1	
S (wt%):	12.0	0.4	0.9	0.5	
Surface area (m²/g):	-	140	137	140	
BCS (MPa):	-	1.60	1.44	1.58	
Average length (mm):	-	3.0	2.8	3.0	
< 2 mm (%):	-	17	20	15	
< 1.5 mm (%):	-	6	10	5	
Fines (wt%):	-	-	-	<0.1	

Metals contaminants:		Notes:
As:	<0.01	
V:	<0.01	
Fe:	0.2	
Si:	0.1	
Na:	0.11	
Ni:	<0.01	

Regenerated densitie		Notes:
CBD (t/m³)	0.843	
SD (t/m³):	0.784	
PDLD (t/m³	0.903	
VF (-):	0.325	

Regen/Lab REACT™:		Notes:
RVA (%):	92	vs fresh
RWA (%):	98	vs fresh
Δp (bar):	1.01	

Performance prediction

Loading parameters

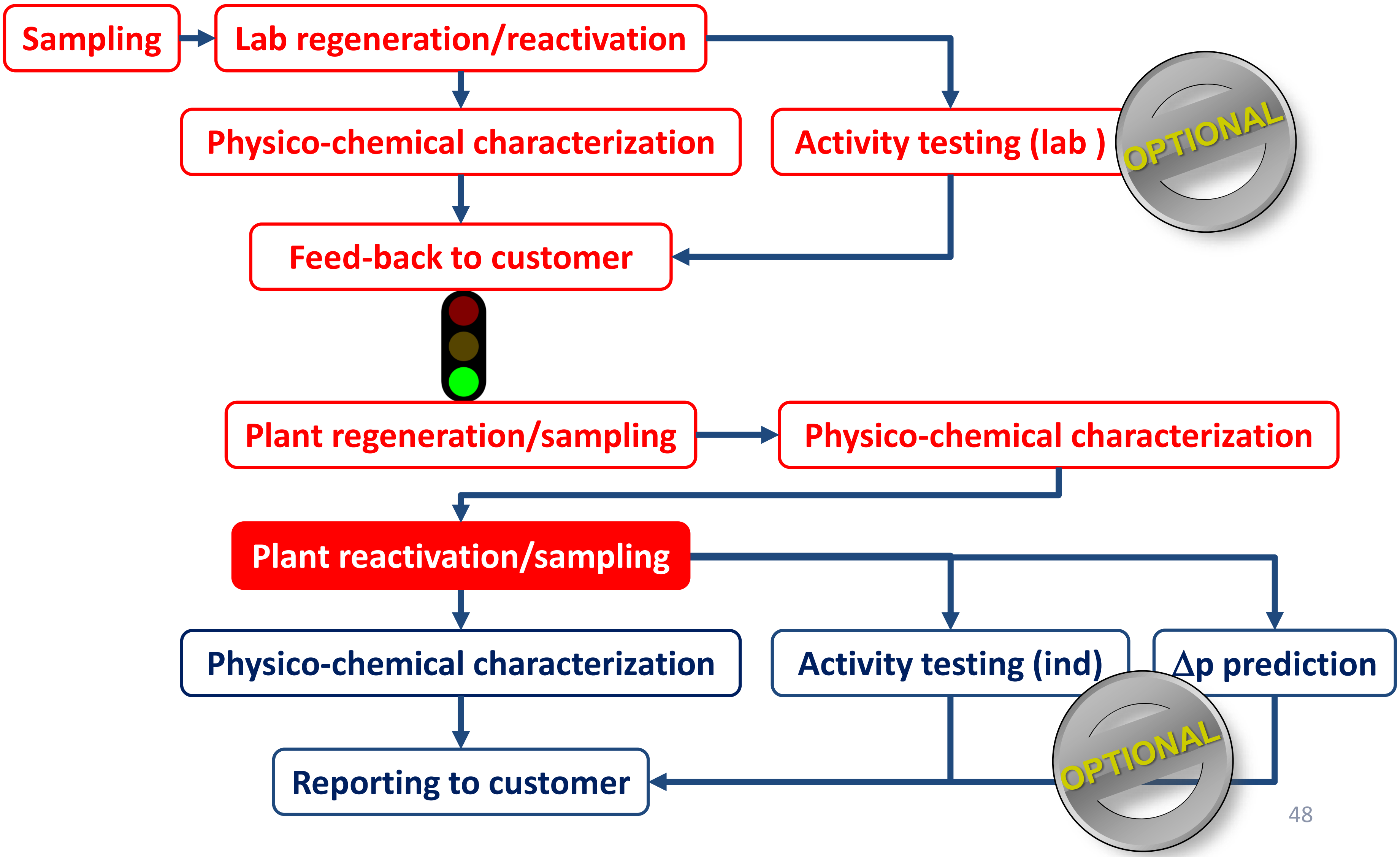
Additional analysis results can be published via a stock database directly accessible via the Internet

1XXXX/A KF757 3Q	Spent:	Lab regen:	Spec:	Regen:	Notes:
LOI (wt%):	18.3	-	-	-	
Smoke test:	Yes	-	-	-	
HC/other volatiles (wt%):		-	-	-	
C (wt%):	14.1	0.1	-	0.1	
S (wt%):	12.7	0.3	-	0.8	
Surface area (m²/g):	-	176	-	170	
BCS (MPa):	-	-	-	1.2	
Average length (mm):	-	-	-	4.8	
< 2 mm (%):	-	-	-	1	
< 1.5 mm (%):	-	-	-	0	
Fines (wt%):	-	-	-	<0.1	

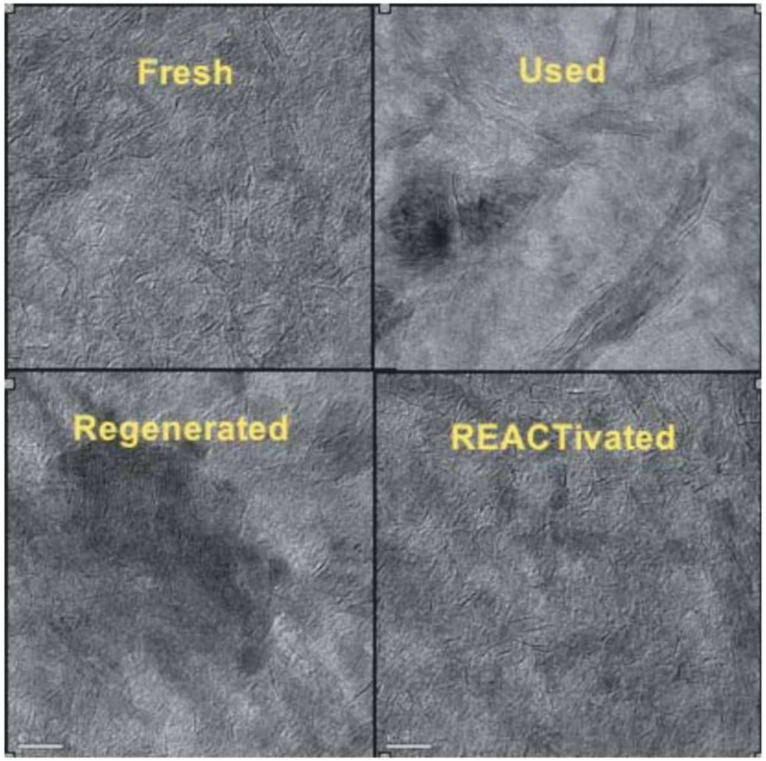
Metals contaminants:		N[illegible]
As:	<0.01	
V:	0.01	
Fe:	0.12	
Si:	0.15	
Na:	0.15	
Ni:	<0.01	

Regenerated densitie		Notes:
CBD (t/m³)	0.727	
SD (t/m³):	0.676	
PDLD (t/m³	0.801	
VF (-):	0.382	

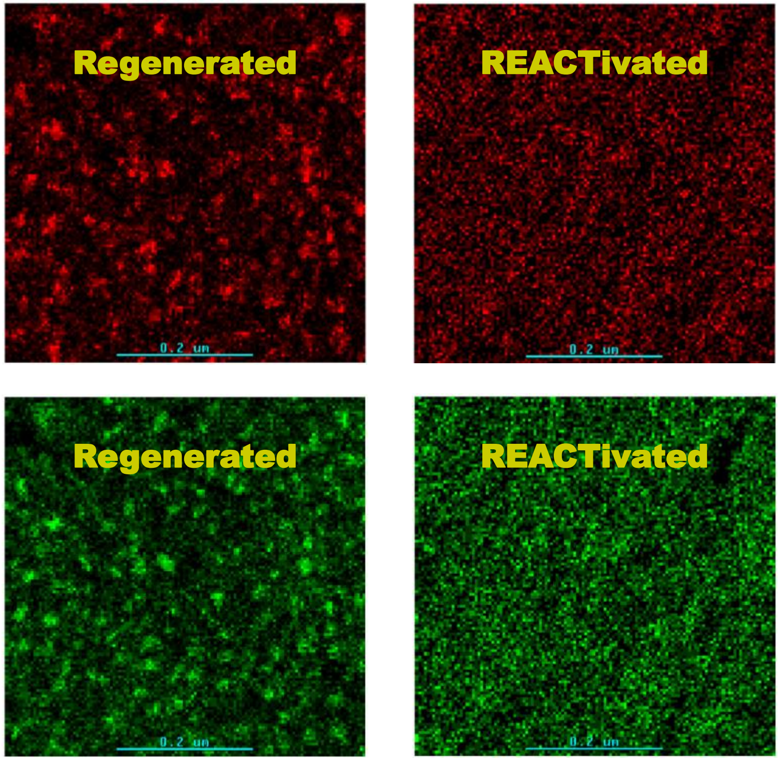
HPC TREATMENT



REACTIVATION: STARS CATALYST



TEM micrograph of CoMo catalyst

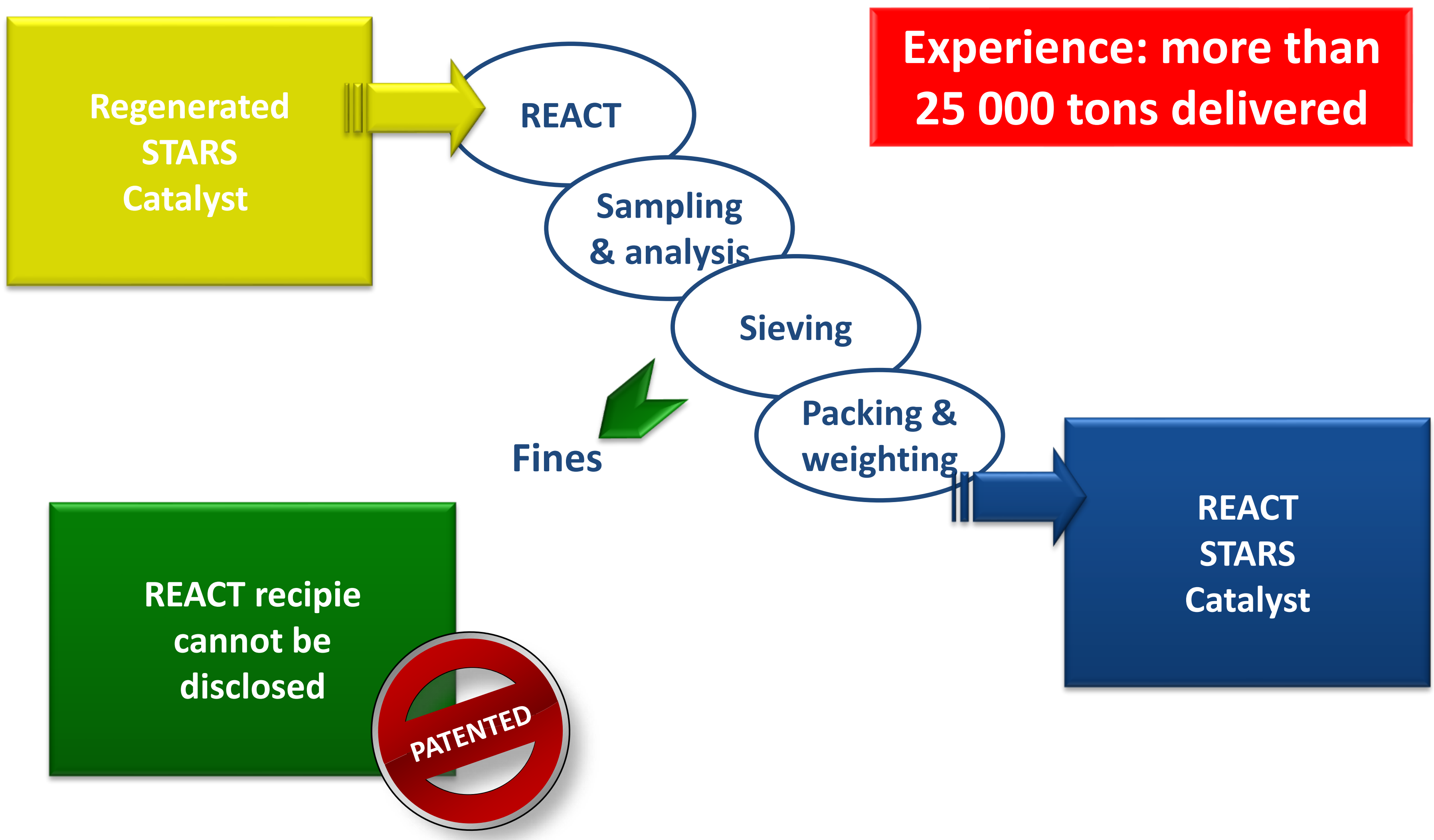


STEM-EDX maps of Co (red) and Mo (green)

Redispersion of the active phase

E. Brevood, Catalysts Courier 60 (2005) 4.
S. Eijsbouts, A.A. Battiston, G.C. van Leerdam, Catal. Today 130 (2008) 361.

EUREACT REACT™ STEPS



REACT report

Comments:

PO number:

1XXXX/A KF767 1.5E

End of treatment: 1/2/2013

Mass balance

Oxidic catalyst:
net: (kg)
42100 43 BB

REACT™ REJUVENATION

REACT™ catalyst:
net: (kg)
50054 43 BB

Catalyst characteristic

1XXXX/A KF767	Specs:	REACT™:	Notes:
C (wt%):	-	-	
S (wt%):	-	-	
Surface area (m²/g):	-	144	
Average length (mm):	2.8	2.85	
< 2 mm (%):	20	19	
< 1.5 mm (%):	10	6	
Fines (wt%):	<1.0	0.2	
BCS (MPa):	-	1.55	

REACT™ densities:		Notes:
CBD (t/m³	1.039	
SD (t/m³):	0.966	
PDLD (t/m	1.111	
VF (-):	0.338	

Loading parameters

	REACT™	Notes:
RVA (%):	95	vs fresh
RWA (%):	101	vs fresh
Δp (bar):	1.04	

Performance prediction

SPECIFIC EURECAT TECHNOLOGIES

Total sulfiding:

- CoMo, NiMo, NiW catalysts (TOTSUCAT)

Reduction:

- Pd, Pt, PtPd, PtRe, PtSn, Ni, Cu, CuZn...

Selectivation:

- Pd, Pt, PtRe, Ni, Activated carbons

Chlorination:

- Pt, PtRe, PtSn, PtPd

Customized treatments:

- Confidential (treaments for various manufacturers and end-users)

Specific Eurecat technologies

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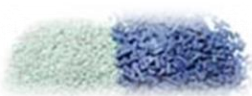
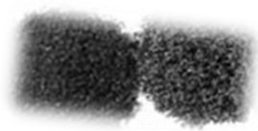
UNIT OPERATION/CATALYST LIFE CYCLE





Fresh → Loading → Startup → Run → Unloading → Regeneration Reactivation

Metal reclaim

~~In-situ sulfiding~~

Activity
Δp

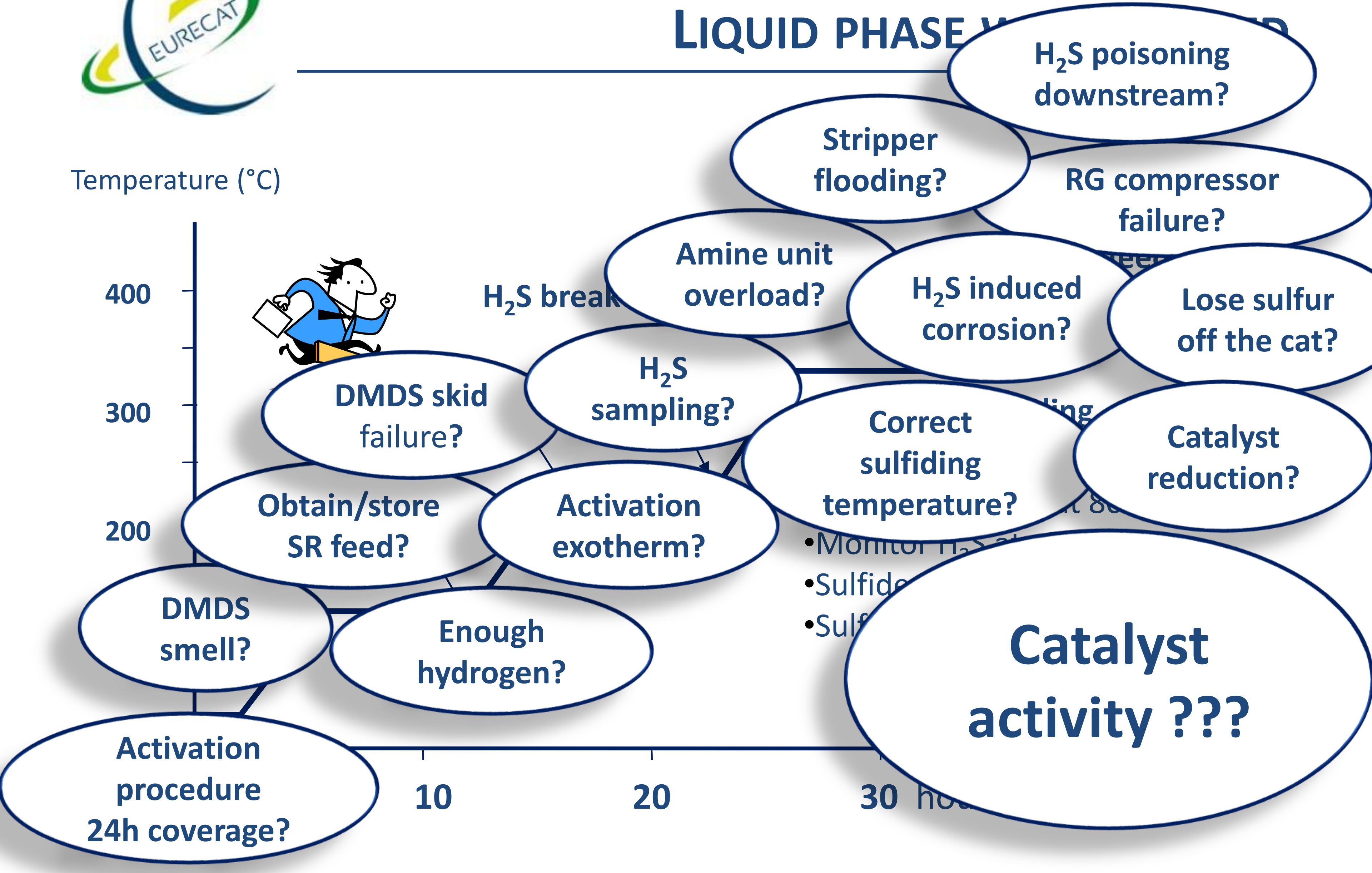
SMARTDUMP
CARBODUMP

Ex-situ Sulfiding: TOTSUCAT

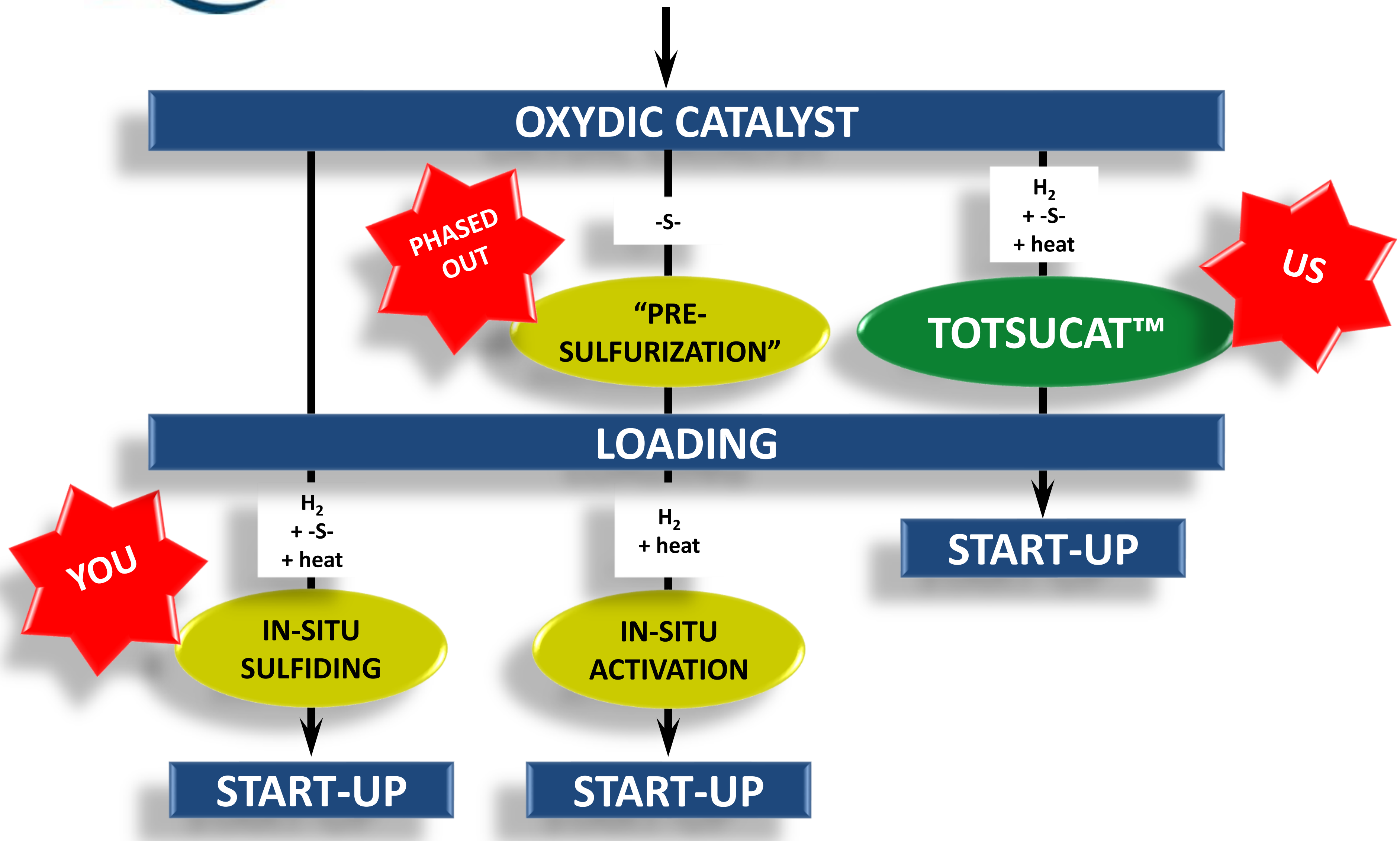
Initial activity
Δp prediction

REUSE
CASCADING
POOL
RESALE

STARTUP WITH IN-SITU SULFIDING
LIQUID PHASE



CATALYST SULFIDING



Totally Sulfided Catalyst (Totsucat) vs Presulphiding (Acticat, Sulficat...)

	TOTSUCAT™	Presulphiding
Catalyst delivered already at full activity?	YES	NO
In situ activation required?	NO	YES
Sulphiding conditions?	Optimized for each catalyst type	Fixed by in situ procedure
Typical start up time	8h	24h+
Need to perform final sulphiding step at 320-350°C (CoMo/NiMo)?	NOT APPLICABLE	YES
Activation exotherm?	NOT APPLICABLE	YES
Additional H_2 required for activation?	NOT APPLICABLE	YES
Typical H_2S level in recycle gas during startup	< 500 vppm	1-2 vol%

TOTSUCAT® Benefits

Easy and quick

No DMDS or other sulfiding chemical to handle

No additional H_2 needed at startup

No activation exotherm

No need to reach final sulfiding temperature

No recycle gas sampling / H_2S monitoring

No impact of H_2S on downstream units

Fail-proof: upsets will not damage the catalyst

Maximum catalyst performance

Typical TOTSUCAT® Applications

Critical Path Units

- Downtime cost for in situ sulfiding often outweighs Totsucat cost.
- Totsucat with Amine passivation for Hydrocrackers saves precious startup time.

Temperature Limited Units

- Some units cannot achieve correct sulfiding temperature: in situ sulfided catalysts will not perform as designed.

Before Sulfur Sensitive Units

- Reformers and Isom units contain precious metal catalysts that are sensitive to H_2S contamination.

Hydrogen Limited Units

- Some units are difficult to sulfide, as there is not enough H_2 available at the time of startup.

TOTSUCAT® Commercial Experience

Hydrotreating

- CoMo, NiMo, NiCoMo

Selective Hydrogenation

- NiMo and CoMo

Pyrolysis Gasoline

- NiMo and CoMo

Hydrocracking

- NiMo and NiW

Lube / Wax Hydrofinishing

- NiMo and CoMo
- NiW

Other…

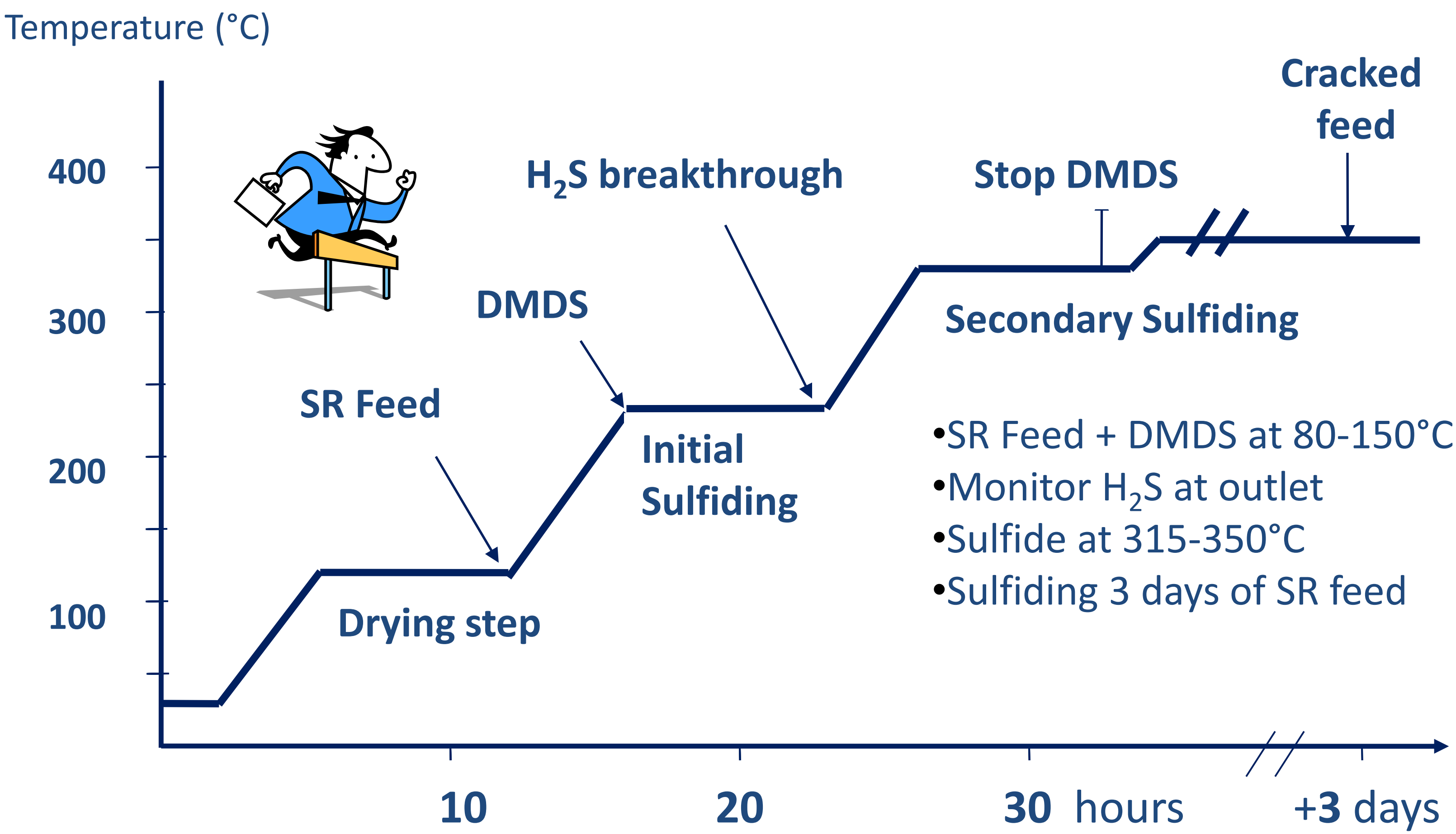
- Biofuels
- Contaminant traps
- …..

Over 1200 Totsucat lots treated worldwide: 30 000 tons of catalyst

TOTSUCAT® BRANDS

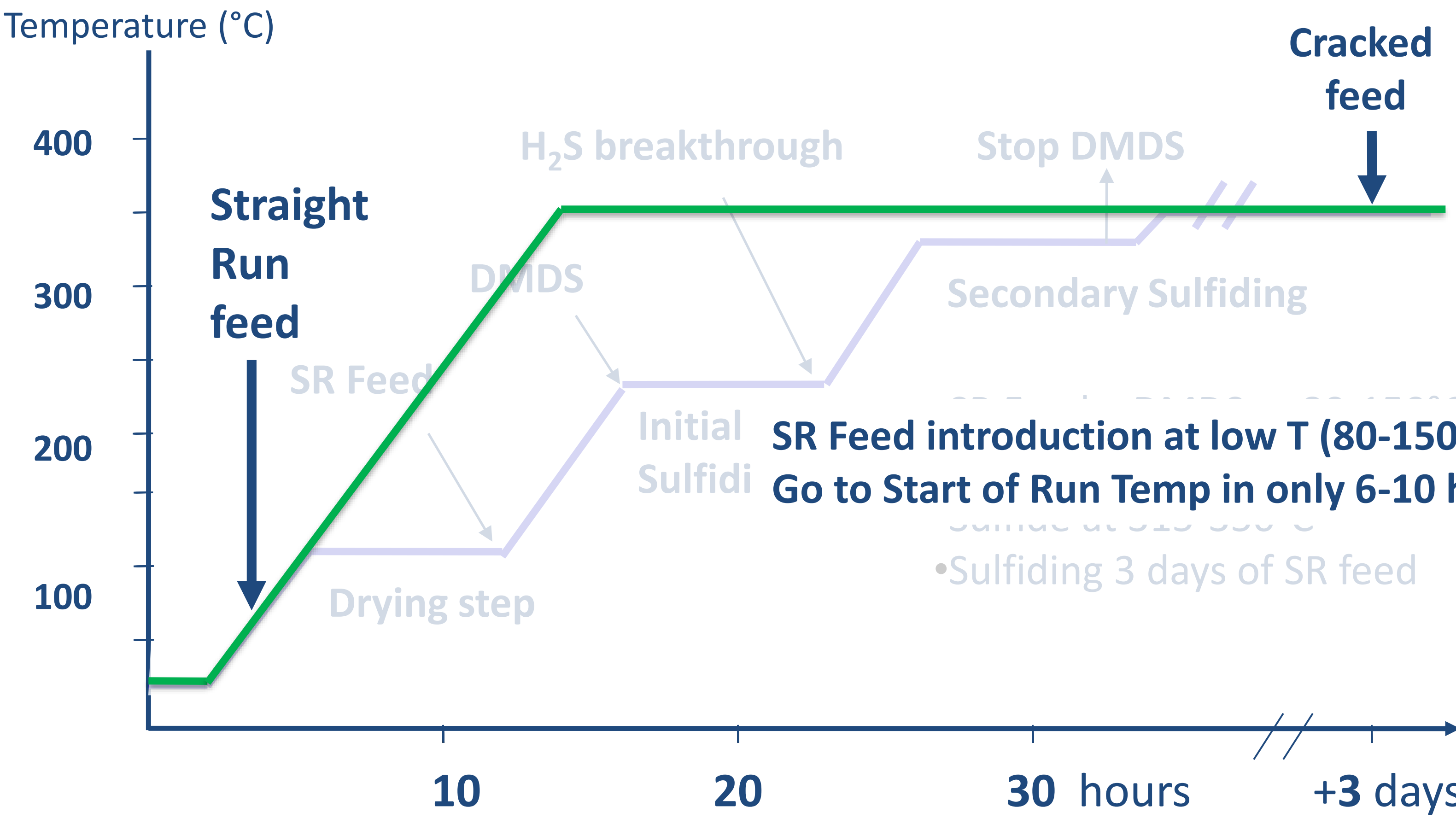
TOTSUCAT – G	• Naphtha, Kero, FCC gasoline, Tail Gas, Lubes
TOTSUCAT – D	• (Ultra Low Sulfur) Diesel
TOTSUCAT – N	• Hydrocracking Pretreat
TOTSUCAT – E	• FCC Pretreat
TOTSUCAT – HC	• Hydrocracking
TOTSUCAT – CFP	• Light Cycle Oil, Heavy Cycle Oil • Coker and Visbreaker Naphtha / Diesel

STARTUP WITH IN-SITU SULFIDING



- SR Feed + DMDS at 80-150°C
- Monitor H_2S at outlet
- Sulfide at 315-350°C
- Sulfiding 3 days of SR feed

STARTUP WITH TOTSUCAT® G/D/E/N/HC



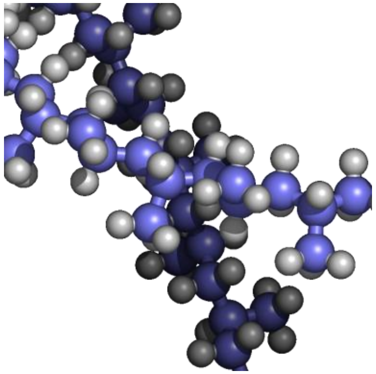
- Startup Liquid phase with SR Feed

ISSUE OF CRACKED FEED

Cracked feed (from Coker, FCC) contains **(di)olefins and aromatics**

Exposed to freshly sulfided catalyst, they **polymerise**

Gums deposits **block** catalyst pores and active sites



Leading to a permanent **loss** in catalytic activity

- **Catalyst manufacturers recommend a break-in period of at least 3 days using straight run feed.** → **Solution: TOTSUCAT CFP**

TOTSUCAT® CFP

CFP = Cracked Feed Protection

- TOTSUCAT®-CFP mimics the 3 days break-in period
- Catalytic acidity is reduced no gums formation
- Can inject cracked feed immediately
- Proven in refineries: 60+ references

Example case of 75 tons reactor treating 30% cracked feed

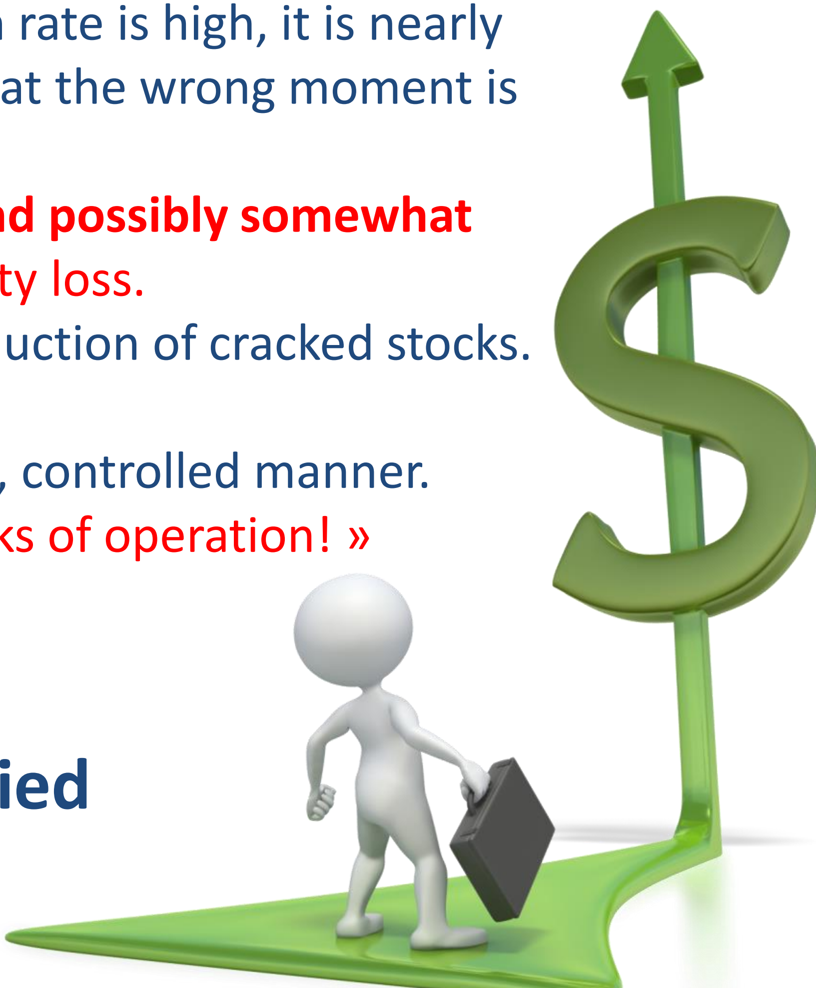
- lost opportunity in order of ~500 k$
- plus associated logisitics cost.

CASE STUDY

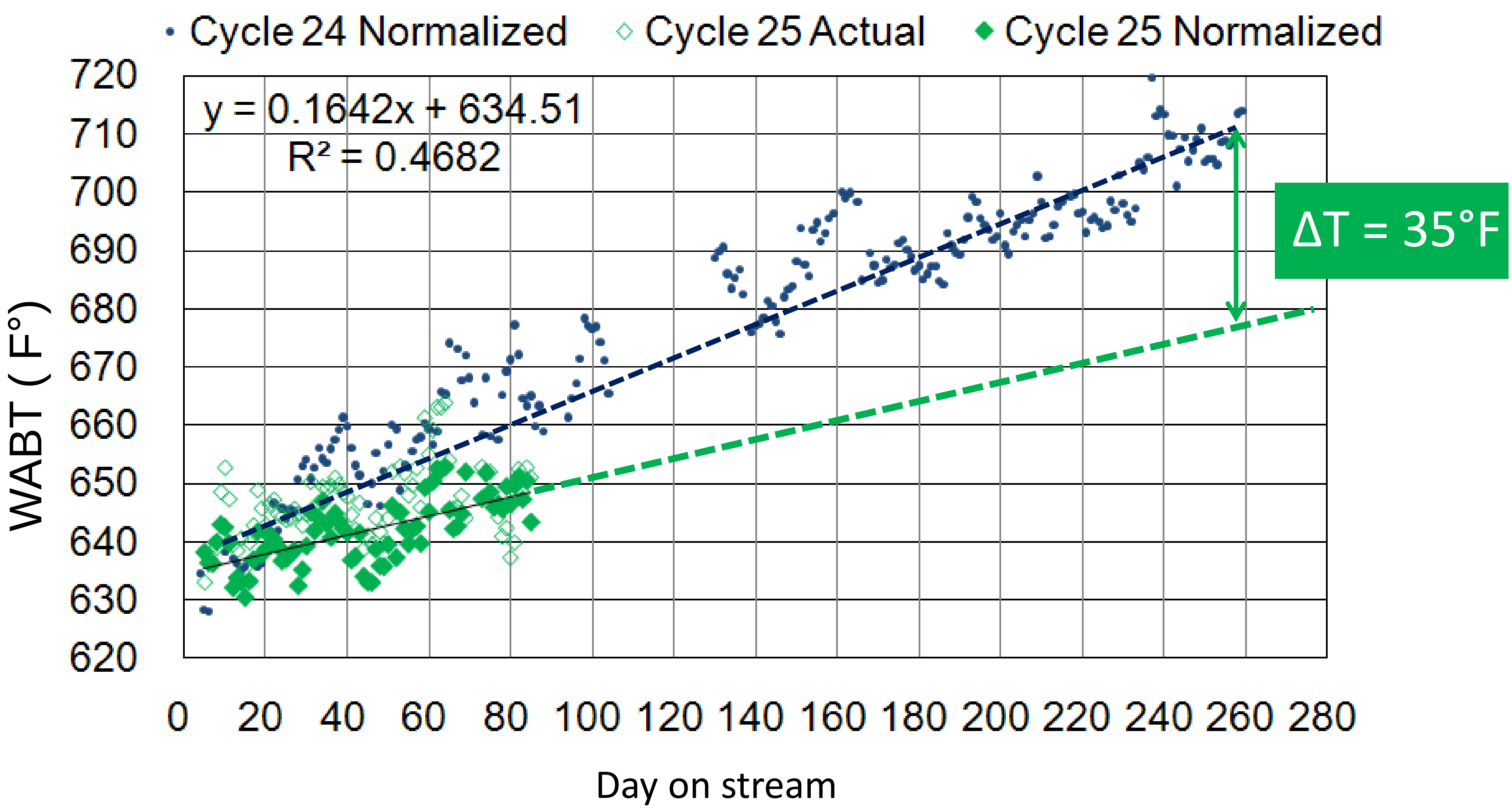
Recommendations from Catalyst Supplier:

- « In a stressed unit, once the deactivation rate is high, it is nearly impossible to reduce it. 2-3 % LCO added at the wrong moment is sufficient to double the deactivation rate.
- Therefore, it is **critical to have a gentle and possibly somewhat lengthy startup** to avoid premature activity loss.
- Run 3 days on virgin oil prior to the introduction of cracked stocks. Longer is better!
- Introduce cracked stocks in a slow, steady, controlled manner.
- **Do not push the unit** in the first two weeks of operation! »

Instead, the refinery applied Totsucat CFP

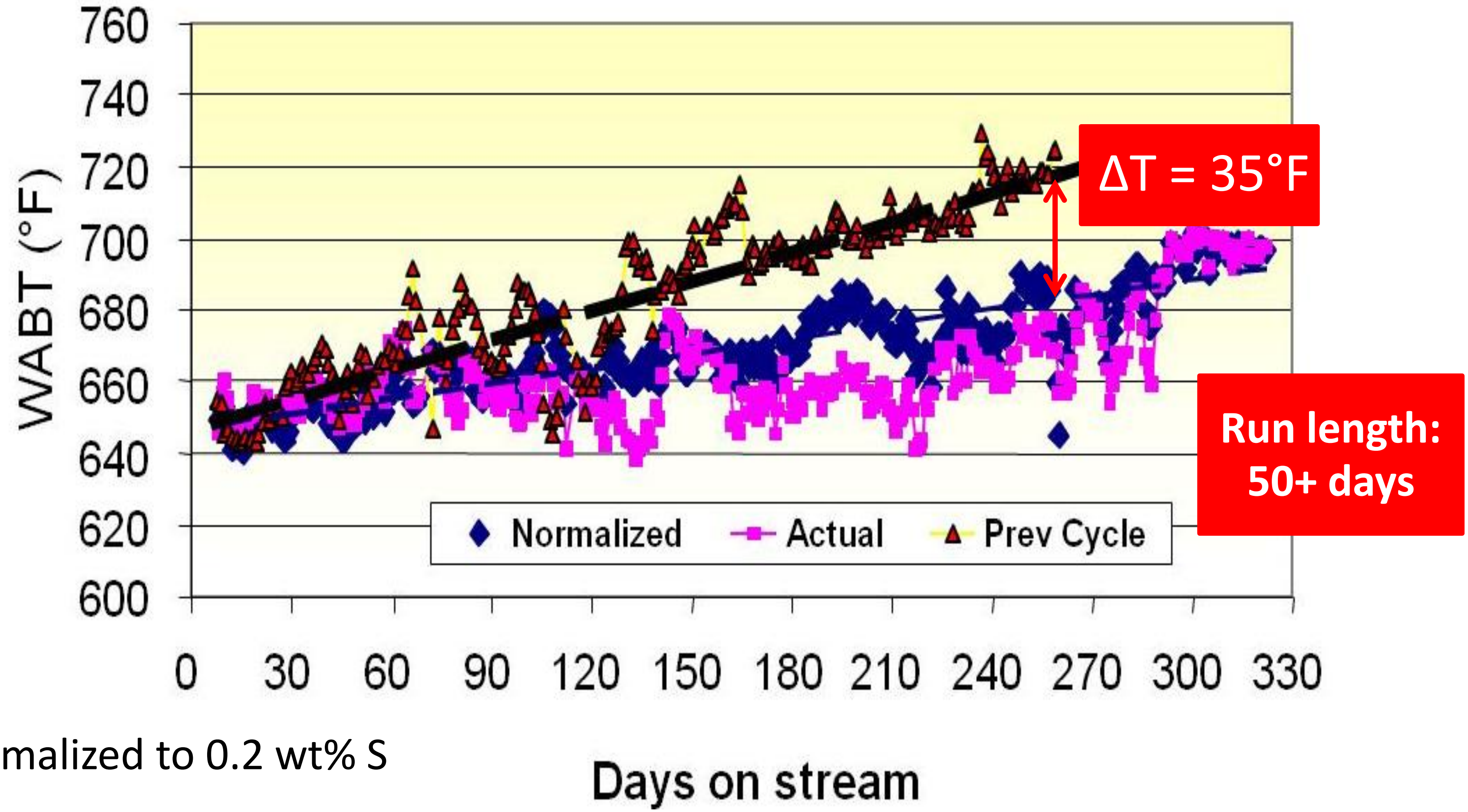


CASE STUDY - TOTSUCAT® CFP IN ULSD
SERVICE AFTER 90 DAYS



Normalized to 0.2 wt% S

CASE STUDY - TOTSUCAT® CFP IN ULSD SERVICE AFTER 320 DAYS



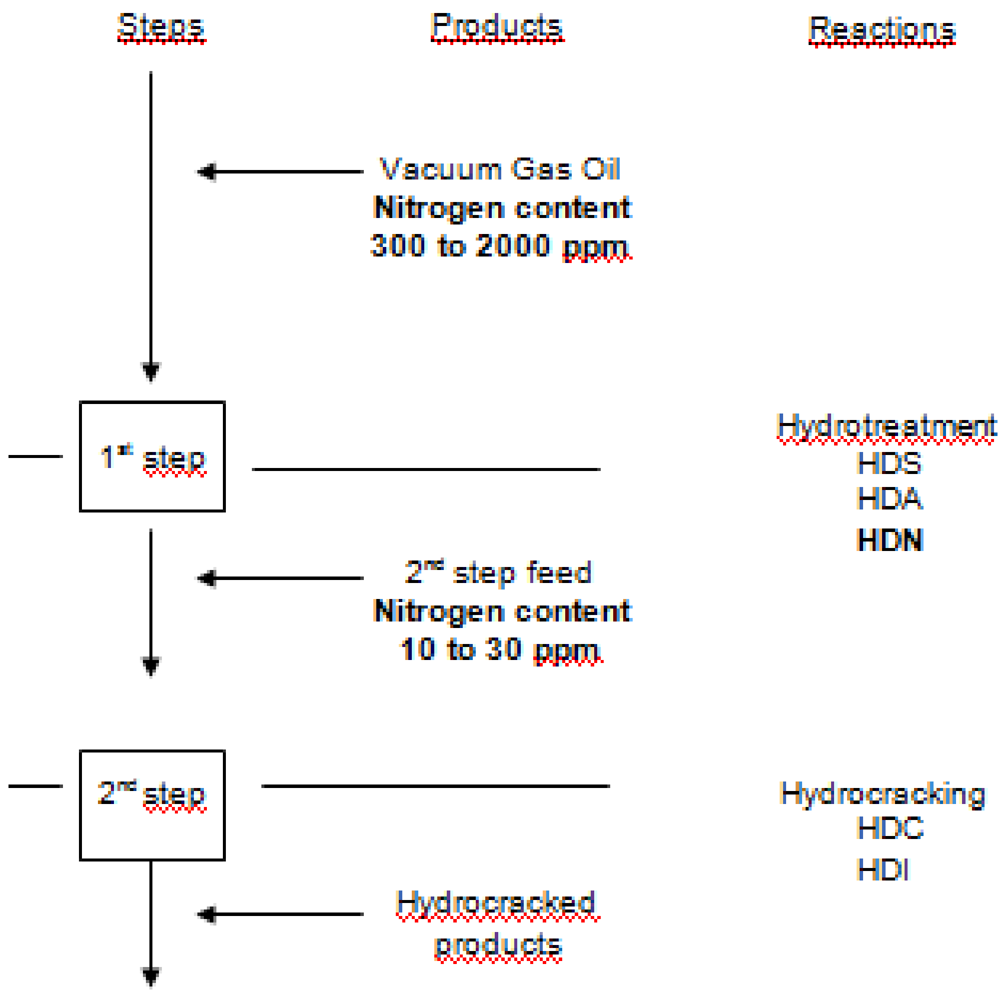
Normalized to 0.2 wt% S

- **Deactivation significantly lower with TOTSUCAT-CFP than with in situ!**

TOTSUCAT ® BRANDS

TOTSUCAT – G	• Naphtha, Kero, FCC gasoline, Tail Gas, Lubes
TOTSUCAT – D	• (Ultra Low Sulfur) Diesel
TOTSUCAT – N	• Hydrocracking Pretreat
TOTSUCAT – E	• FCC Pretreat
TOTSUCAT – HC AP Acidity protection	• Hydrocracking
TOTSUCAT – CFP	• Light Cycle Oil, Heavy Cycle Oil • Coker and Visbreaker Naphtha / Diesel

HYDROCRACKING PROCESS: 2 STEPS OF REACTIONS

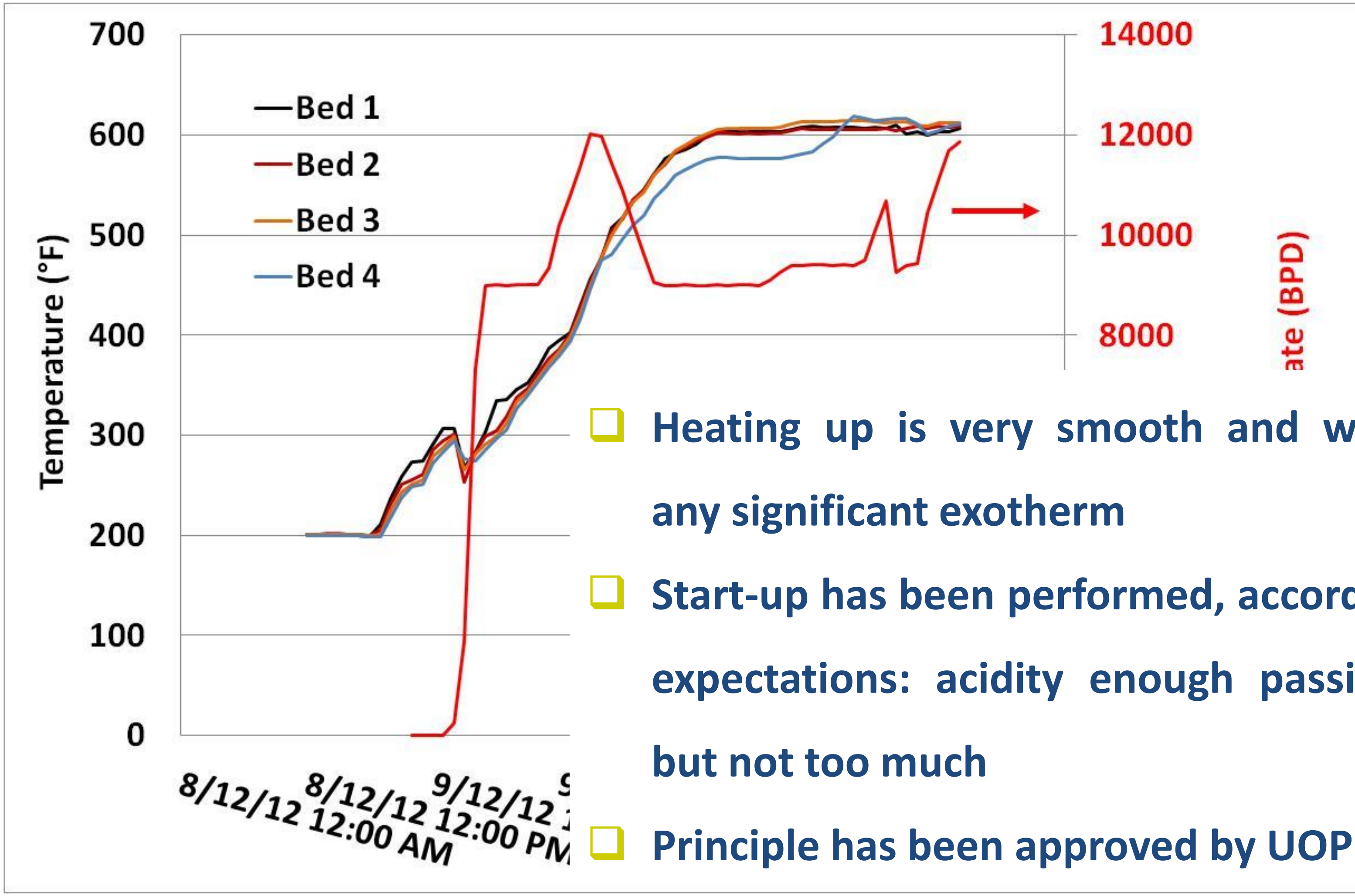


HDC: ISSUE OF START-UP

- **Fresh vs steady state catalysts**
  - Zeolite catalyst contains very strong acidic sites: can crack hydrocarbons already around 250°C
  - In steady state, the strongest acidic sites are essentially covered with N containing compounds (mainly ammonia) cracking temperatures are between 300 and 350°C.

- **How to go from a fresh to a steady state catalysts?**
  1. Wait for a long time that N in the feed, transformed by HDN to NH_3, slowly saturates the acidic sites
  2. Inject during sulfiding procedure NH_3 or another N containing compound
  3. **Use the TOTSUCAT HC-AP**

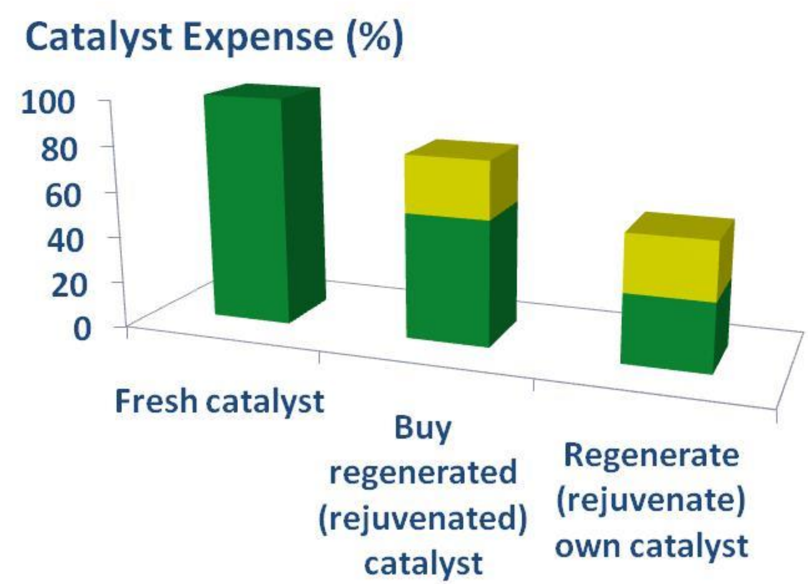
HYDROCRACKER START-UP WITH TOTSUCAT HC-AP



- Heating up is very smooth and without any significant exotherm
- Start-up has been performed, according to expectations: acidity enough passivated, but not too much
- Principle has been approved by UOP

CONCLUSIONS

- Catalyst regeneration and reuse allows to drastically reduce expense:



- TOTSUCAT:
  - Optimise catalyst performance
  - Reduce unit downtime

REGULAR CUSTOMERS

Catalyst manufacturers

Catalyst end-users: oil refiners & (petro)chemicals companies

REGULAR CUSTOMERS

Catalyst manufacturers

THANK YOU FOR YOU ATTENTION!