LUKOIL
OIL COMPANY

Utilization of e-cat flushing to control metal contamination and/or in emergency situation caused by cyclones failure

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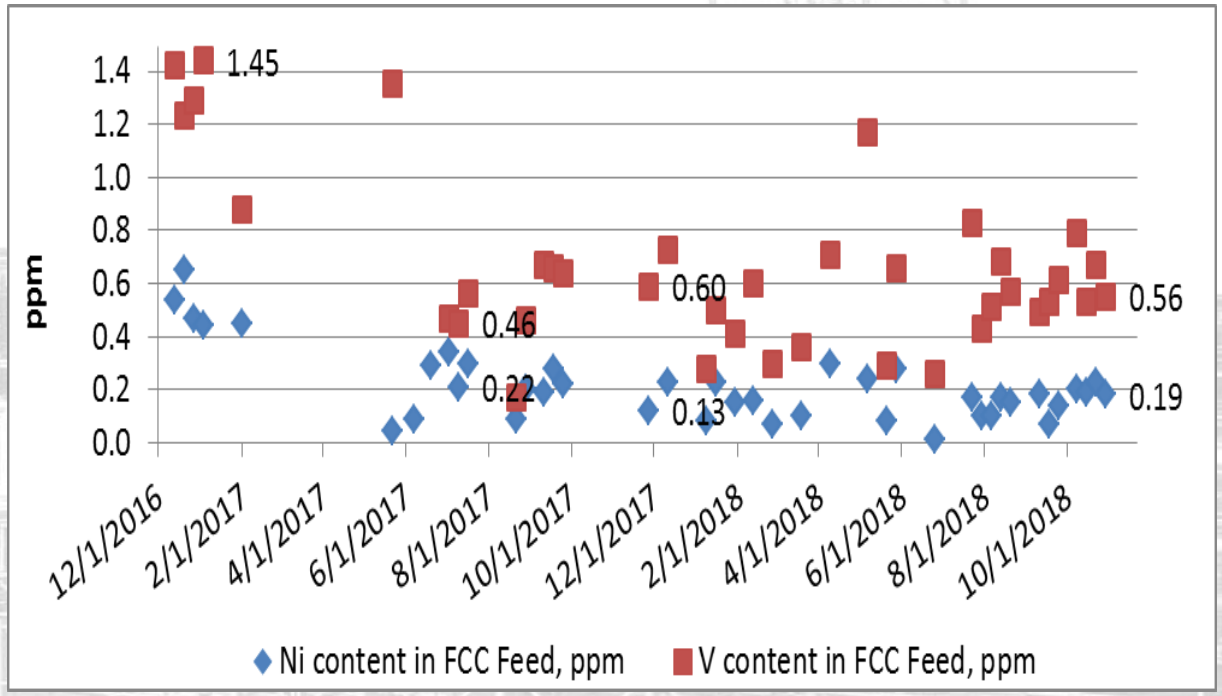
New challenges for FCC Units

- With the greater processing of heavy crude oils in refineries, the importance of fluid catalytic cracking unit has been increased;
- Metals content in heavy feeds is one of the limiting factors in FCCUs, as increased levels of metals lead to high coke and dry gas yields;
- However, processing heavy oil streams in FCCUs also leads to increased distillate yields and improved margins;
- Lukoil Petrotel is not exception of the world trends.

Petrotel-Lukoil FCCU Feed Quality

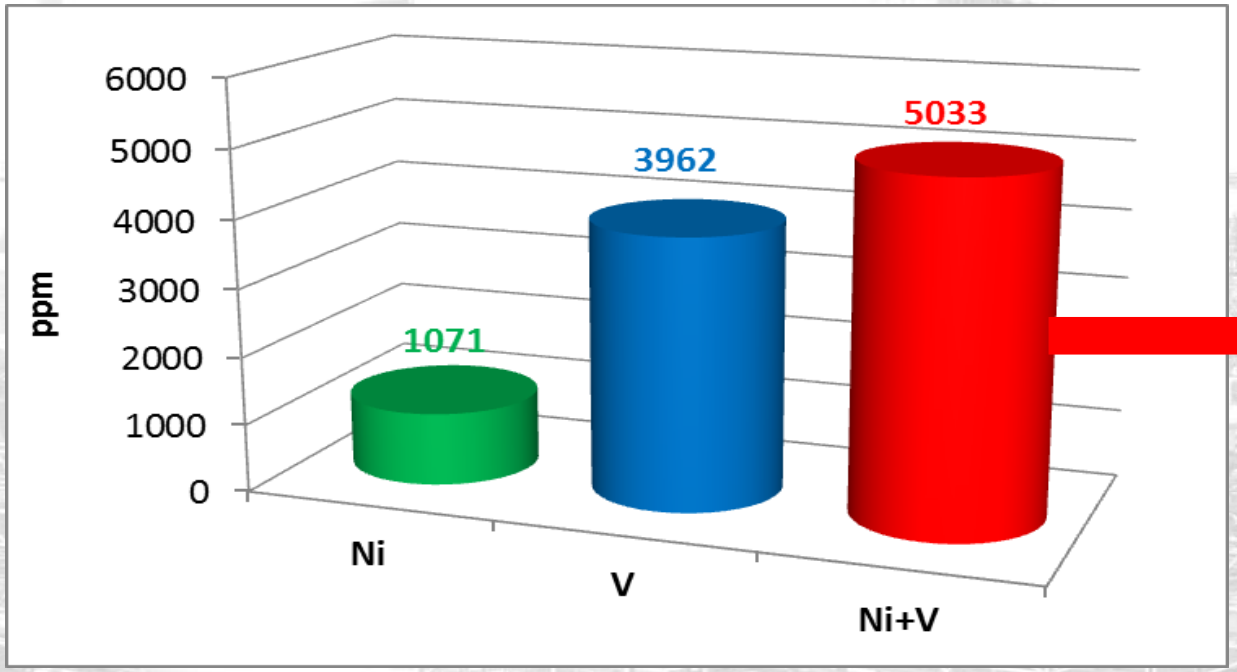
Petrotel-Lukoil FCCU is processing a non-hydrotreated feed (VGO + HCGO) with high contaminants content (S, N, Ni and V):

No.	Properties	Unit	Values
1	Density	Kg/m3	916 – 930
2	Sulphur	%	1.6 - 1.8
3	Nitrogen	ppm	1400 - 1900
4	Ni	ppm	≤ 0.66
5	V	ppm	≤ 1.45
6	IFB / FBP	ºC	320/575
7	Coke Conradson	%wt	0.4 – 1.2



Ni and V contamination of FCC e-cat

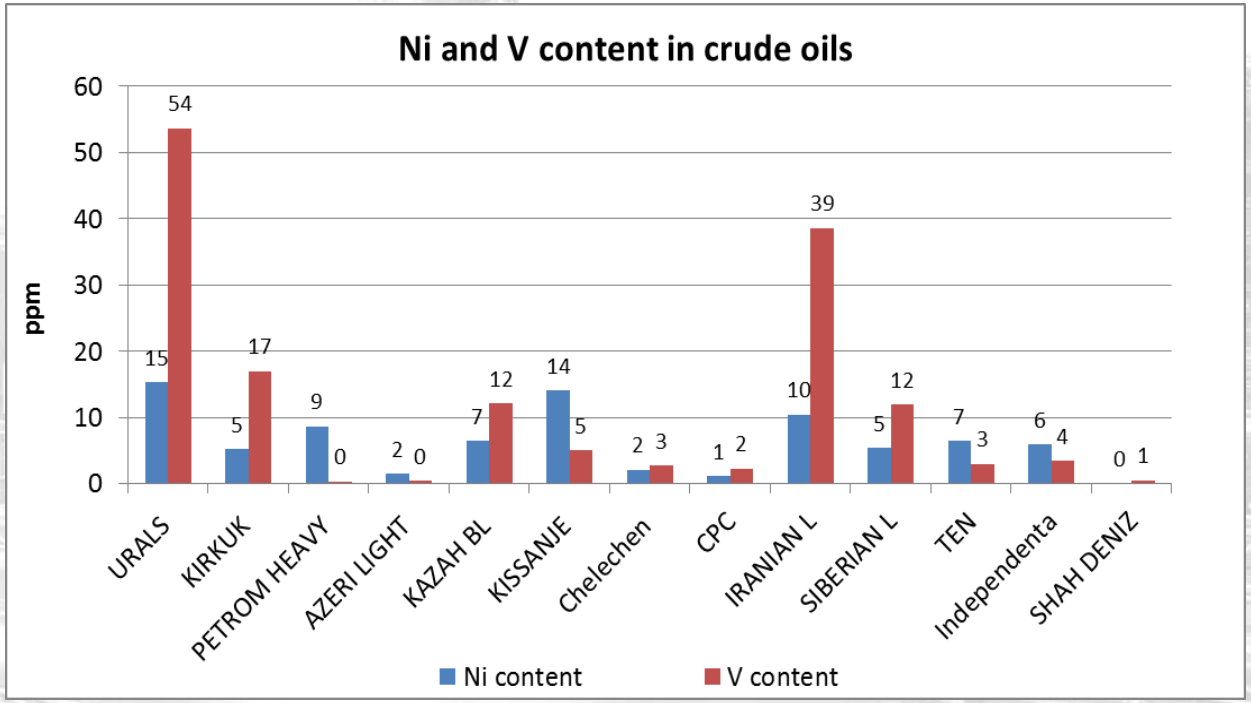
Processing a heavy feed led to contamination/poisoning of e-cat with Nickel and Vanadium:



ECONOMIC LOSSES

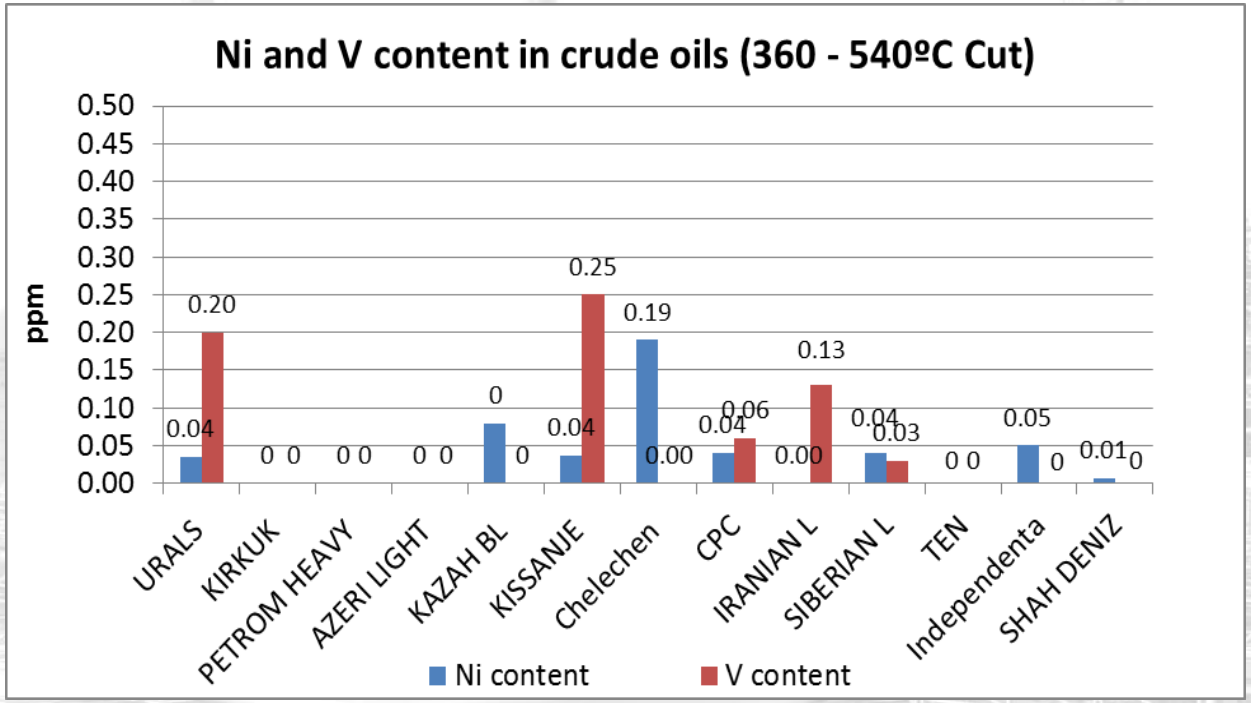
Ni and V content in different crude oils

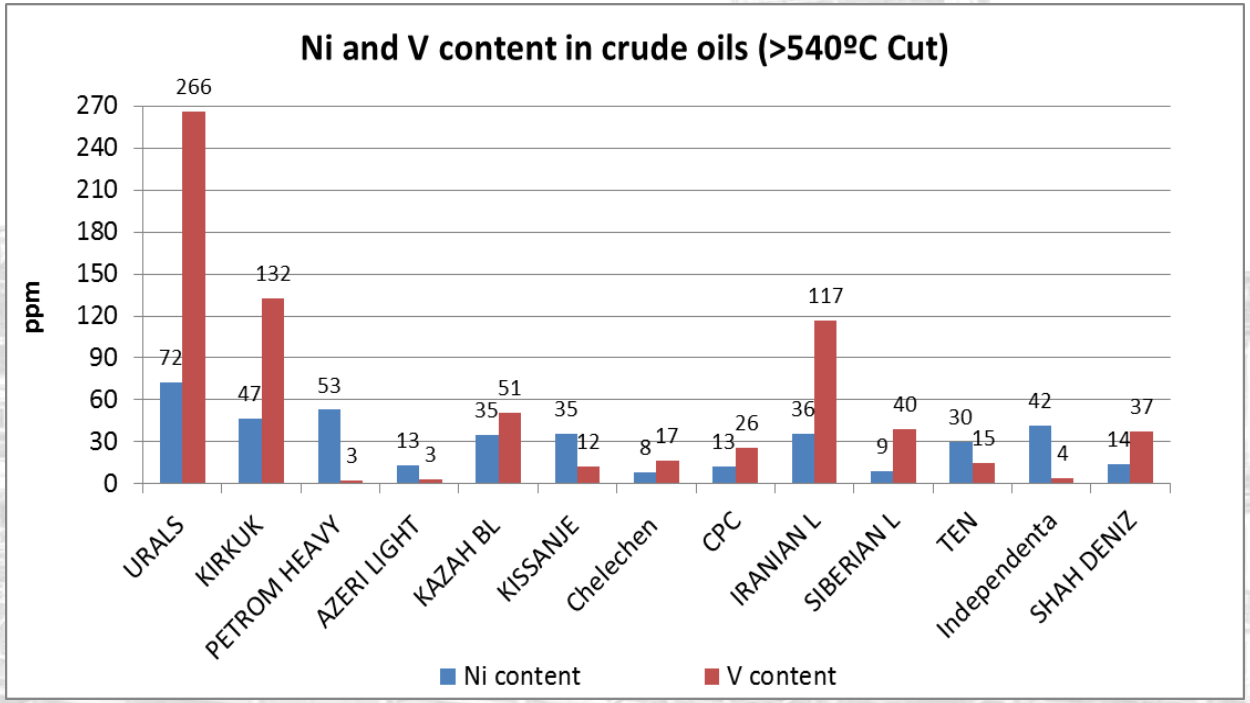
- Crude oils have different metal content depending on their source;
- Crude oils must be selected depending on refinery targets but also on the refinery constraints;
- If metals are affecting the refinery catalytic processes then it is recommended to select and process crude oils with lower metal content;



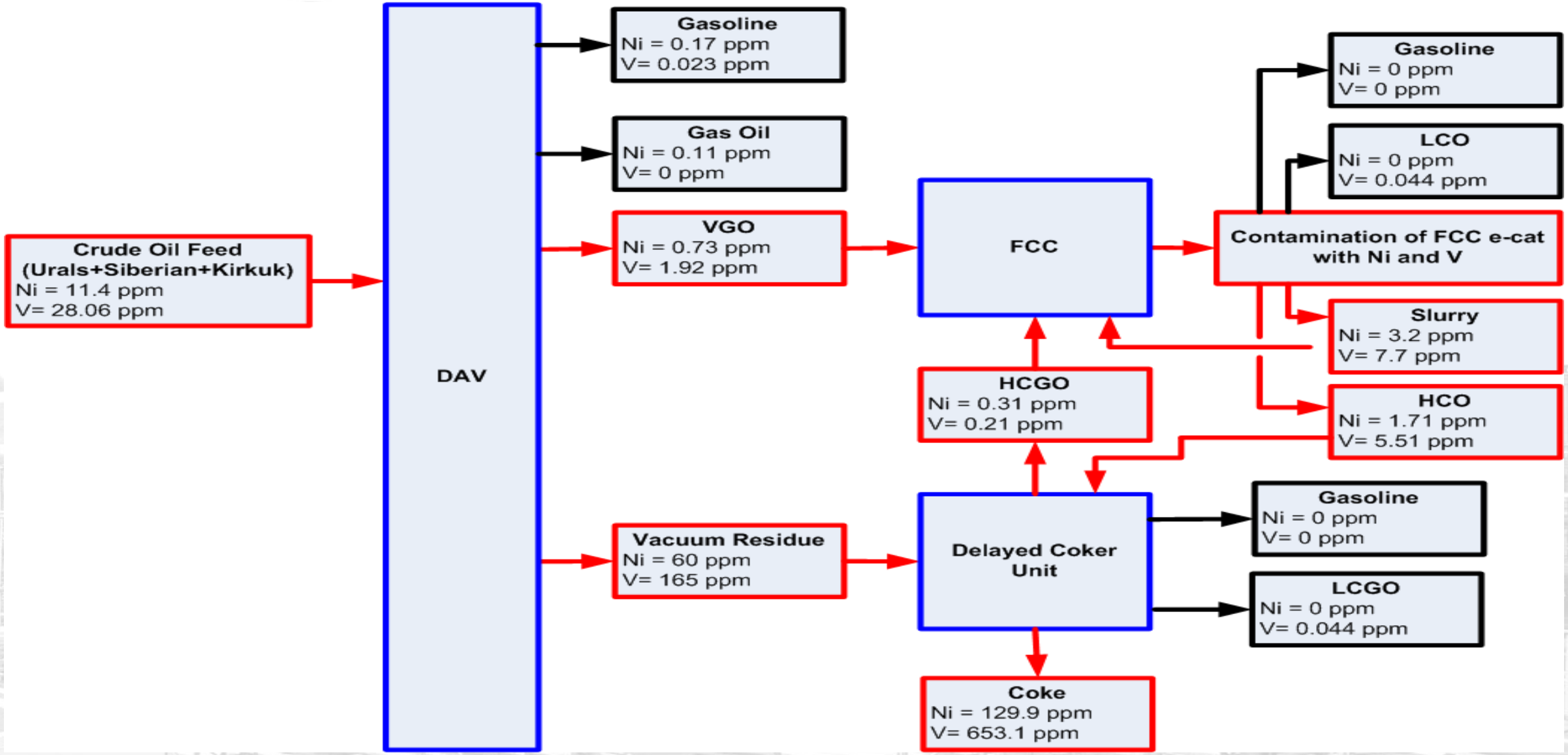
Ni and V content in different crude oils

- Ni and V is concentrated in the >540ºC Cut: VGO (Dist. 90% = 540ºC, FBP = 575ºC) and Vacuum Residue (DCU feed).





Study of Ni and V distribution of refinery process flows



FCC e-cat contamination with Ni and V

No.	FCC catalyst	Ni + V	FACT wt%	TSA m^2/g	ZSA m^2/g	REO wt.%	0-20μ	0-40μ	APS
1	Fresh catalyst	0	76	295	185	1.5	2	12	75
2	FCCU e-cat	5033 ↗	65.5 ↘	135 ↘	90 ↘	1.5	0	4	78

Nickel:

- Deposits on catalyst particles;
- Dehydrogenation activity leading to increased hydrogen and coke yields.

Vanadium:

- Deactivate the catalyst causing activity reduction;
- Increases hydrogen and coke yield;
- Destroys the zeolite (especially in the presence of Na).

FCC e-cat contamination with Ni and V

In order to reduce metal contamination the refinery implemented the following solutions:

1. E-cat flushing of FCCU inventory to replace the contaminated e-cat;

2. Optimization of fresh catalyst addition.
   Fresh catalyst dosage rate was increased from 0.6 to 1 kg/t in order to maintain constant the level of Ni and V on FCCU e-cat;

3. Reformulation of fresh catalyst in order to increase its resistance at high Ni and V contamination.

E-cat flushing of FCCU inventory

No.	FCC catalyst	FACT wt.%	TSA m^2/g	ZSA m^2/g	REO wt.%	0-20μ	0-40μ	APS	CO Promoter
1	Fresh catalyst	76	295	185	1.5	2	12	75	Pd
2	FCCU e-cat	65.5	135	90	1.5	0	4	78	Pd
3	Proposed e-cat	73.3	173	118	1.74	1	9	75	Pt

Advantages of using the selected e-cat for flushing:

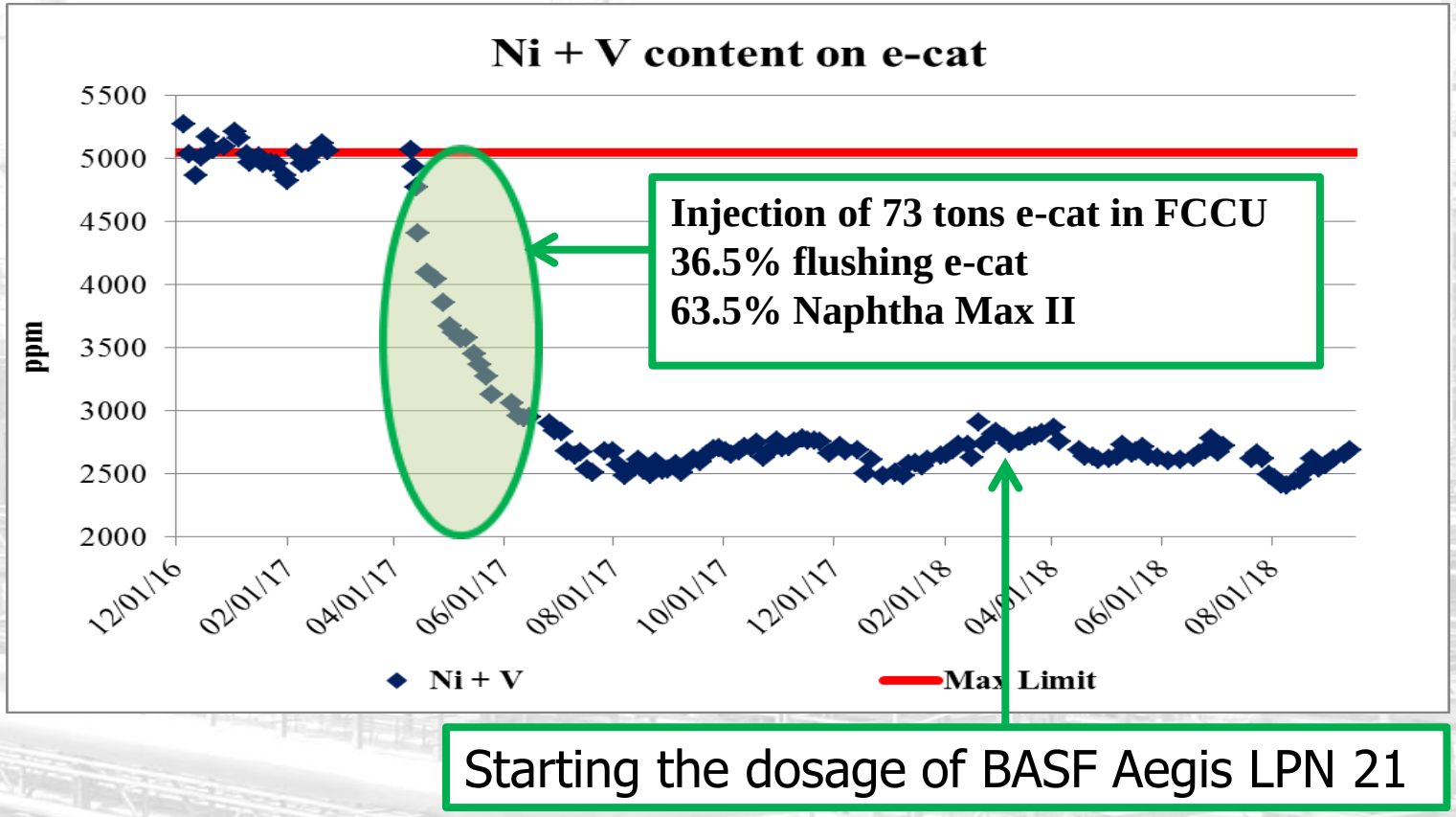
- ✓ Lower cost for procurement in comparison with fresh catalyst;
- ✓ Good quality in comparison with other e-cat types: FACT, TSA, ZSA, REO, APS;
- ✓ The selected e-cat is promoted with ZSM 5.

Disadvantages of using the selected e-cat for flushing:

- ➢ The e-cat is pre-blended with Pt-CO Promoted which will have a negative impact on NOx emissions.

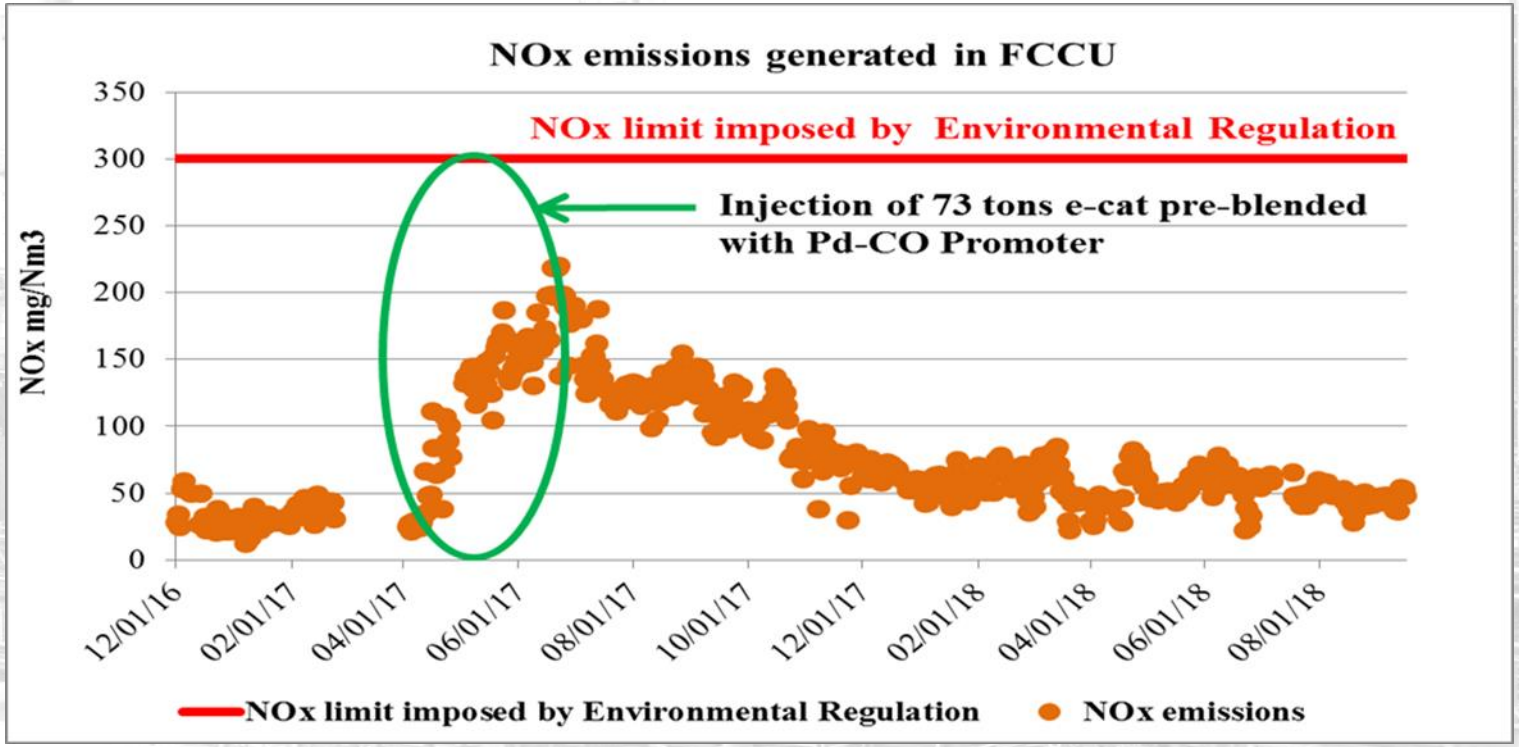
E-cat flushing of FCCU inventory

The refinery decided to inject the proposed e-cat in 6 different batches in order to replace the contaminated catalyst from FCCU inventory but to avoid the increasing of NOx in Flue Gas.



E-cat flushing of FCCU inventory

Dosing a catalyst pre-blended with Pt-CO Promotor increased the NOx emissions in FCCU Flue Gas up to 220 mg/Nm3 (below the maximum allowed limit imposed by Environmental Regulation – 300 mg/Nm3).



Effect achieved by reducing Ni and V content on e-cat

FCC UNIT Products	Unit	Material Balance 5030 ppm Ni+V	Material Balance 2640 ppm Ni+V	Δ -2390 ppm Ni +V
Dry Gas	wt.%	6.93	5.98	-0.95
Propane		1.57	1.78	+0.20
Propylene		4.22	4.56	+0.34
Total C4		8.37	10.60	+2.24
Gasoline		44.58	46.05	+1.47
LCO		19.42	17.31	-2.11
HCO		9.16	8.26	-0.90
Coke		5.44	5.15	-0.29
Losses		0.31	0.31	0.00
Conversion	wt.%	71.42	74.43	+3.01
Economic Effect	**$/t feed**	1.92		

*Note: the Economic Effect was calculated based on refinery RPMS model.

Selection of a more metal resistant catalyst

The refinery organized a tender to select a more metal resistant catalyst (higher zeolite and REO content) for a 3 year contract.

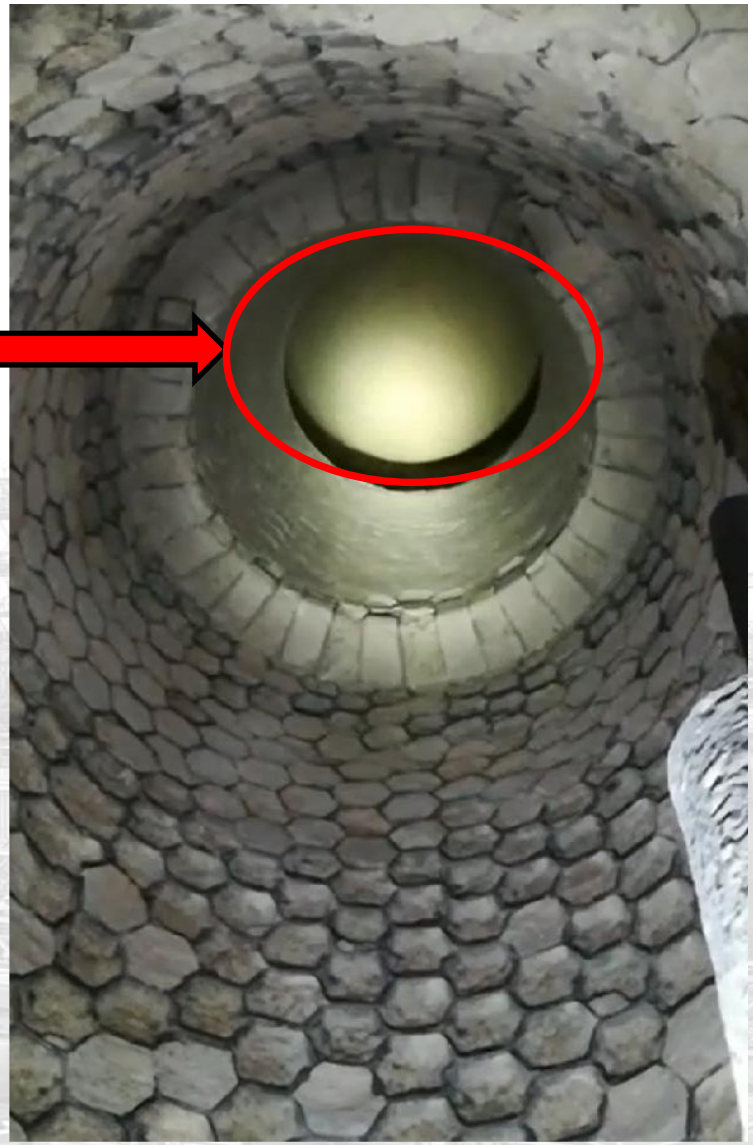
No.	Fresh catalyst characteristics	unit	Naphtha Max II	Aegis	Δ
1	FACT	wt.%	76	77	+1
2	ZSA	m^2/g	185	205	+20
3	MSA	m^2/g	110	85	-25
4	TSA	m^2/g	295	290	-5
5	REO	m^2/g	1.5	1.8	+0.3
6	Low NOx-CO Promoter		Mandatory	Mandatory	

Usage of e-cat in FCCU emergency situation

- Cyclones failure (cracks, plugging, etc) are causing massive e-cat losses which consequently lead to FCCU emergency shut-down;
- If immediate unit shut-down is not possible than is needed to increase the catalyst addition rate in order to compensate the e-cat losses from FCCU system;
- To reduce the operational cost it is recommended to maintain the regenerator catalyst level by dosing e-cat instead of fresh catalyst.

Usage of e-cat in FCCU emergency situation

ECONOMIC LOSSES



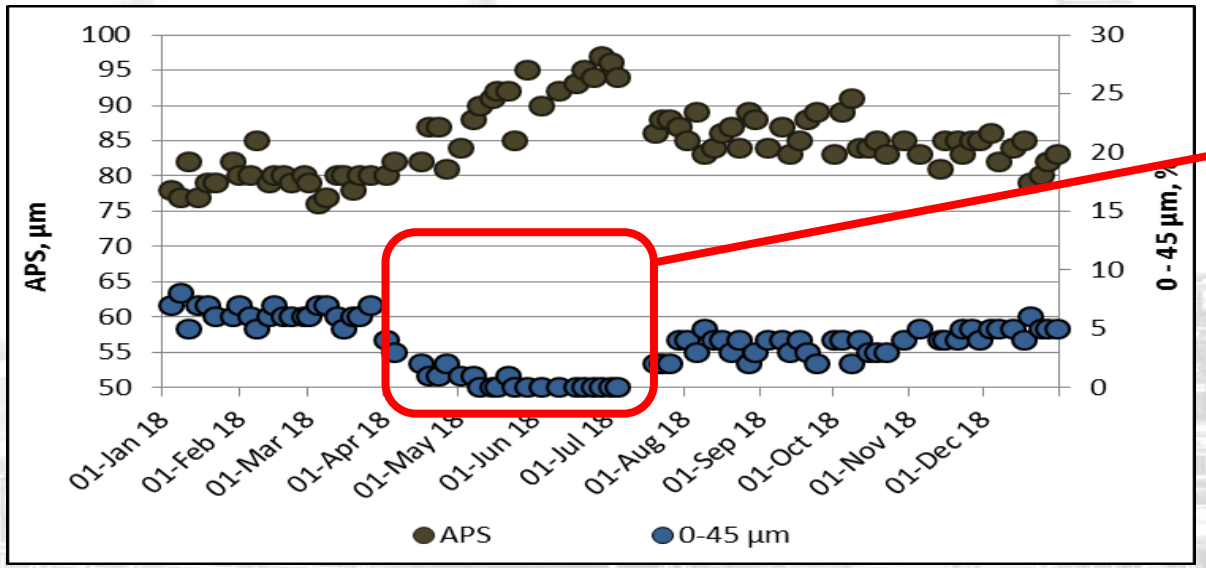
Utilization of e-cat in emergency situation caused by cyclones failure

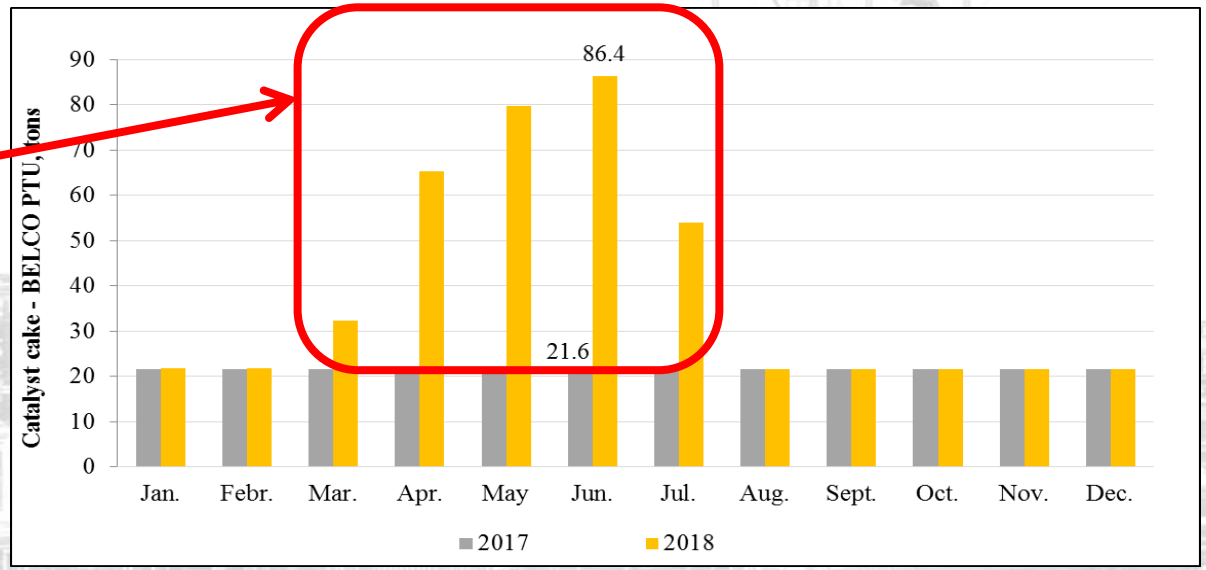
Cyclones failures can be detected easily by doing the following actions:

- Monitoring the FCCU regenerator level;
- Evaluation of e-cat quality: absence of e-cat fines is caused by cyclones inefficiency/failure;
- Monitoring of particulates content in Flue Gas (if there is an on-line analyzer on Flue Gas stack);
- Monitoring the quantity of catalyst collected in Flue Gas Treatment Unit (Wet Scrubbing System, ESP, etc).

Usage of e-cat in emergency situation caused by cyclones failure

- The FCCU engineers noticed a decreasing of regenerator level in the conditions of maintaining the same fresh catalyst addition rate;
- Increasing of APS and complete loss of 0 - 45μ fines;





- Increasing of catalyst quantity collected in BELCO Flue Gas Treatment Unit;
- FCCU shut-down for regenerator inspection was planned in July (in order to achieve the Production Planning targets);

Utilization of e-cat in emergency situation caused by cyclones failure

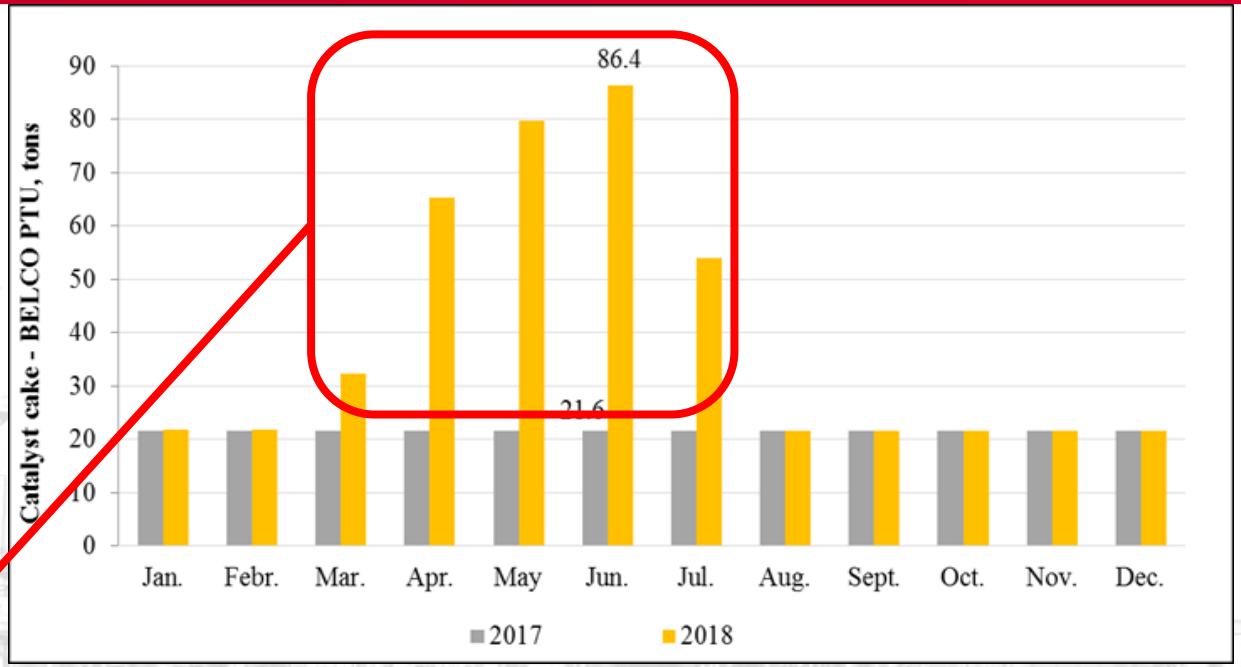
- During FCCU regenerator inspection it was found that 2 cyclones (2nd stage) were plugged.

Functional cyclone

Plugged cyclone

Utilization of e-cat in emergency situation caused by cyclones failure

- In case of cyclones failure it is recommended to compensate the catalyst losses by dosing e-cat instead of fresh catalyst.



Filter cake collected in BELCO Unit (35% catalyst content)	Catalyst losses	Economic Effect
tons	tons	$
211	74	203,382

*Note: The procurement cost presented for catalyst are estimative and can vary depending on catalyst supplier or the type of catalyst supplied.

Conclusions

- Processing a heavy, non-hydrotreated feed (VGO+HCGO) can lead to the contamination of FCC equilibrium catalyst with Ni and V;
- Ni and V has a poisoning effect on FCC e-cat and increases the hydrogen and coke yields. Also vanadium deactivate the catalyst causing activity reduction;
- The most efficient method that can be implemented for a rapid reduction of Ni and V content is e-cat flushing (taking into consideration the procurement cost);
- Reduction of Ni and V content with -2394 ppm by e-cat flushing increased the FCCU conversion with 3.01 wt. %. Consequently were increased the yields in Propane (+0.20%), Propylene (+0.34%), C4 Cut (+2.24%) and Gasoline (+1.47%). Also were reduced the yields in Dry Gas (-0.95%), LCO (-2.11%), HCO (-0.90%) and Coke (-0.29%);
- The Economic Effect achieved by reducing Ni and V contamination was estimated by the refinery at ~1.92 $/t feed;

Conclusions

- It is important to evaluate the quality of the e-cat proposed to be used for flushing in order to not affect the FCC efficiency;
- To avoid the continuous accumulation of Ni and V it is recommended to increase the catalyst dosage rate and adapt it to the feed quality;
- Reformulation and/or selection of a more metal resistant catalyst;
- Cyclones failure can cause massive e-cat losses which consequently lead to FCCU emergency shut-down. If immediate unit shut-down is not possible it is recommended to compensate the catalyst losses by dosing low cost e-cat instead of fresh catalyst;
- In a refinery case (2 cyclones plugged) the economic effect achieved by dosing e-cat instead of fresh catalyst in order to maintain in operation the FCCU (until the planned shut-down) was estimated at ~200.000 $;
- All refineries should have an e-cat stock for FCCU emergency situations.

Thank you for your attention!