SOx ADDITIVE EFFECTS ON FCC EMISSIONS

MİRAY GENÇ

REFCOMM BUDAPEST
2-5 Oct 2017

TUPRAS REFINERIES

İZMİT (1961)

Capacity: 11 million tons

Nelson Complexity: 14.5

Personnel: 1923

Storage: 3.1 million tons

İZMİR (1972)

Capacity: 11 million tons

Nelson Complexity: 7.66

Personnel: 1353

Storage: 2.51 million tons

TUPRAS REFINERIES

KIRIKKALE (1986)

Capacity: 5 million tons

Nelson Complexity: 6.32

Personnel: 865

Storage: 1.4 million tons

BATMAN (1955)

Capacity: 1.1 million tons

Nelson Complexity: 1.83

Personnel: 463

Storage: 0.253 million tons

GENERAL INFORMATION FOR FCC UNITS

REFINERY	İZMİT	İZMİR
Licensor	UOP	UOP
S/U year	1972	1978
Design Capacity (Sm^3/day)	1750	2225
Maximum Operating Capacity (Sm^3/day)	2250	2400
Feed Properties	HVGO, UCO API: Min 19-20 IBP=350-380 ^oC FBP =550-590 ^oC Concarbon: 0.6 wt.%	HVGO, UCO, DAO, Lube Oil Extracts API: Min 19-20 IBP=350-380 ^oC FBP =550-590 ^oC Concarbon: 0.85 wt.%

REGULATIONS

	SO_x, mg/Nm^3 (3% O_2)	NOx, mg/Nm^3 (3% O_2)	Particulates, mg/Nm^3 (3% O_2)
BAT			
New FCC Units	≤300	<30-100	10-25
Old– Full Burn FCC Units	100-800	<100-300	10-25
Old– Partial Burn FCC Units	100-1200	<100-400	10-25

Local regulations?

Refinery bubble concept?

Best available techniques limits?

FCC SOx REDUCTION

Options with high operating / investment costs

Crude choices

Feed pretreatment

Scrubbers & crystallisation units

or

ADDITIVES?

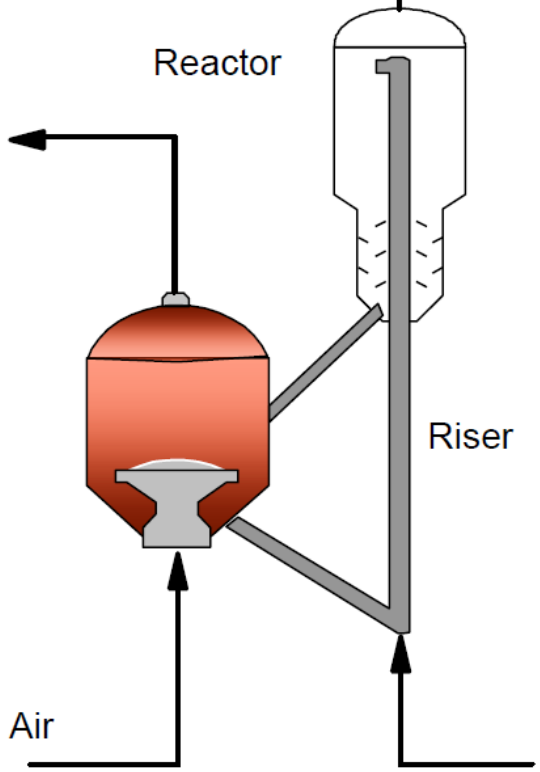
FACTORS AFFECTING ADDITIVE PERFORMANCE

Additive performance is unit specific!

- Feed sulfur,
- Good air distribution in regenerator ,
- Excess oxygen,
- Regenerator temperatures,
- Catalyst circulation rate,
- Stripper performance,
- Inventory,
- Fresh catalyst addition,
- Lift gas H_2S content

affect the performance of the additives.

SULFUR BALANCE



Products:

Light Gas:	H_2S (20-60%)
Gasoline:	2-10%
LCO:	10-25%
Bottoms:	5-35%
	~ 90 - 98%

Flue gas

SOx: 2-10%

S (in coke) 2-10%

$SO_2 + ½ O_2 \leftrightarrow SO_3$

(90%) (10%)

Feedstock

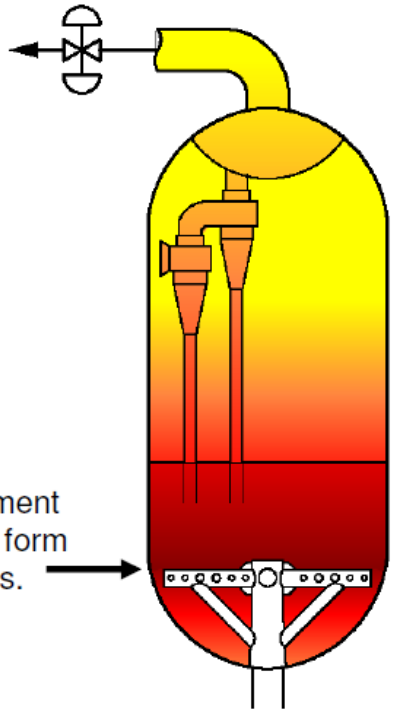
Sulphur: 0.3-3.0 wt%

Figure by: Grace

SULFUR SPECIES IN REGENERATOR

Partial Burn

- COS, CS_2
- H_2S
- SO_2
- SO_3



Oxidizing environment around air grid will form oxidized species.

Full Burn

- SO_2
- SO_3

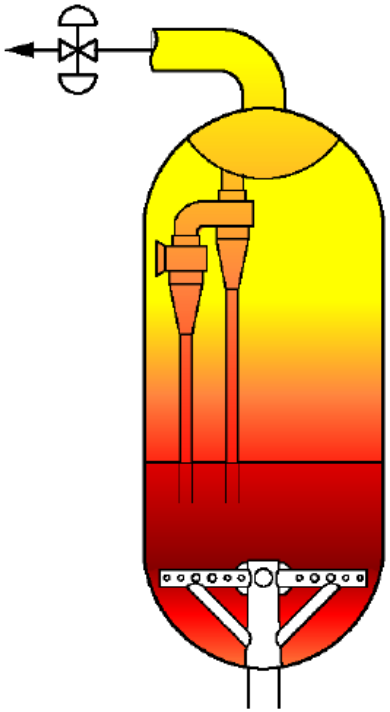
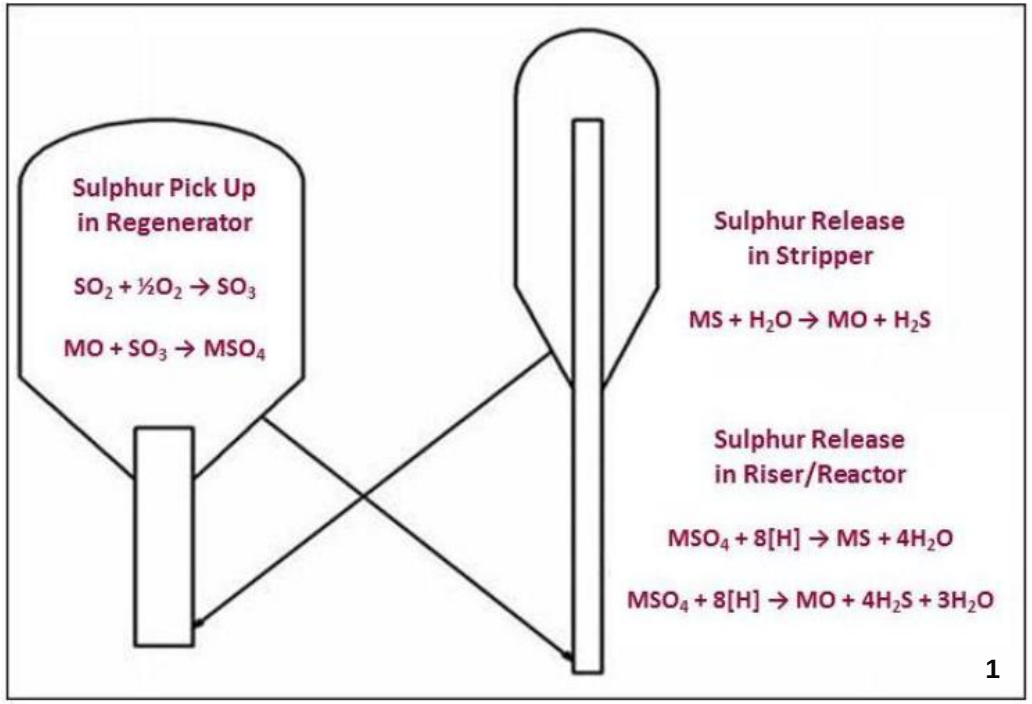
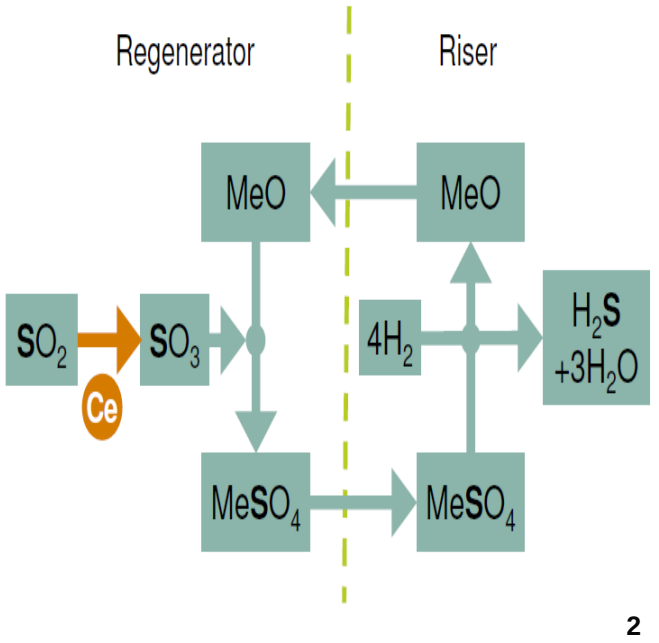


Figure by: Grace

SOx ADDITIVE MECHANISM – FULL BURN





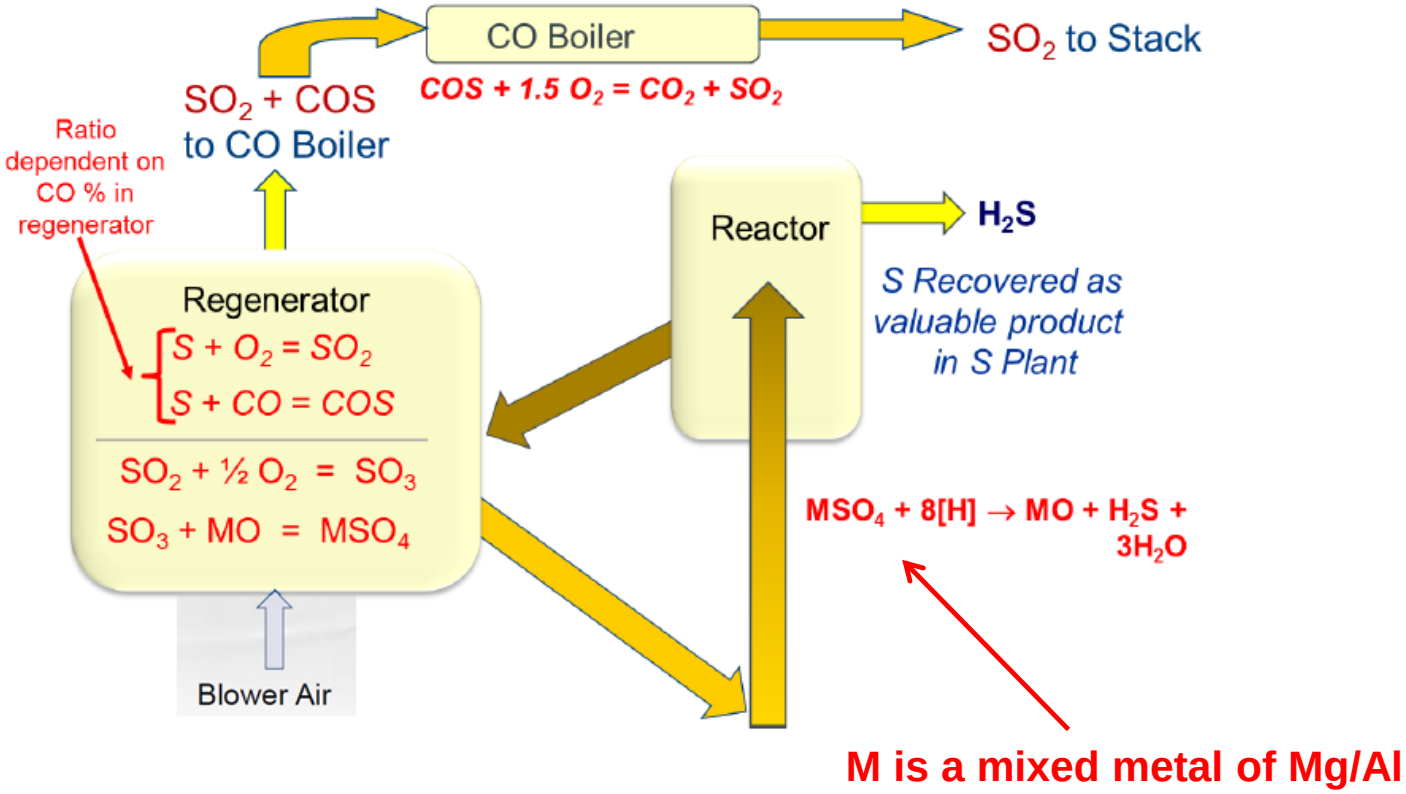
M is mixed Mg/Al oxide.

Cerium is effective in the formation of SO_3.

Vanadates form H_2S from S and release in the reactor.

Figure by: Intercat (1) & Albemarle (2)

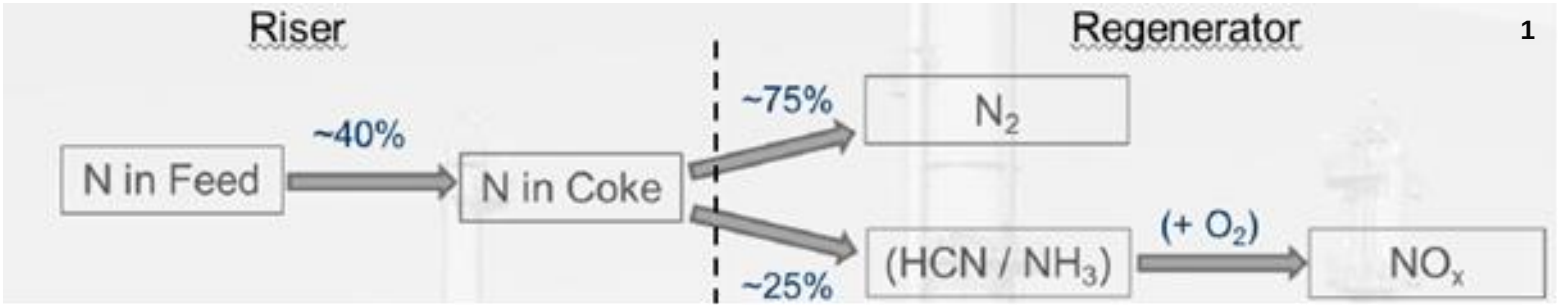
SOx ADDITIVE MECHANISM – PARTIAL BURN



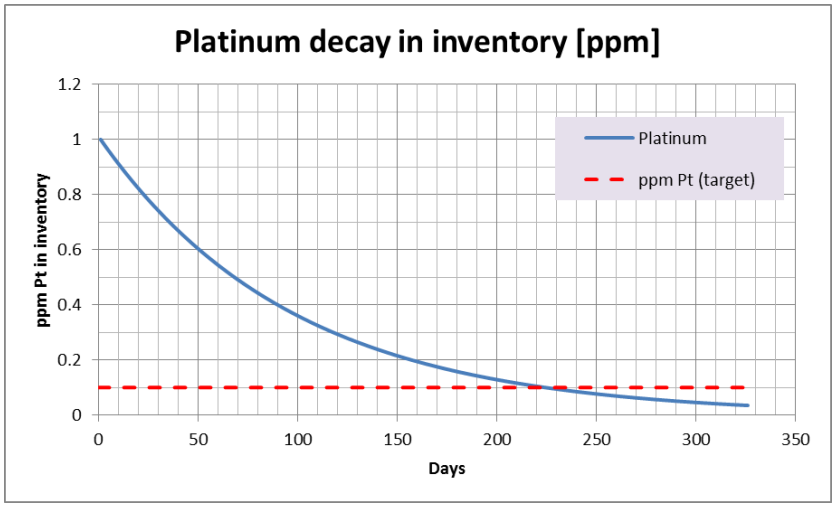
Check CO to CO_2 ratio in regenerator. Additives must have minimum effect on CO:CO_2 balance.

Figure by: Intercat

NOx FORMATION



Consider using CO promoters, Pt – Pd based or preblended catalysts?



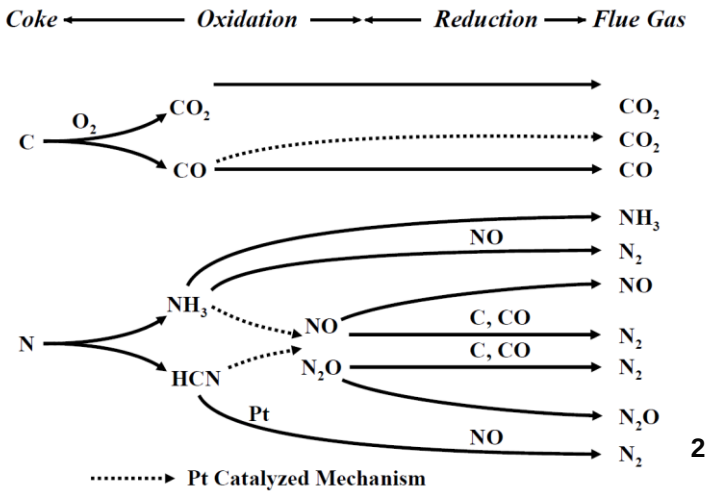


Figure by: Intercat (1) & UOP (2)

ADDITIVE LOADERS

Single Addition System

Multi-Compartment System (left)

Figure by: Intercat

ADDITIVE LOADERS

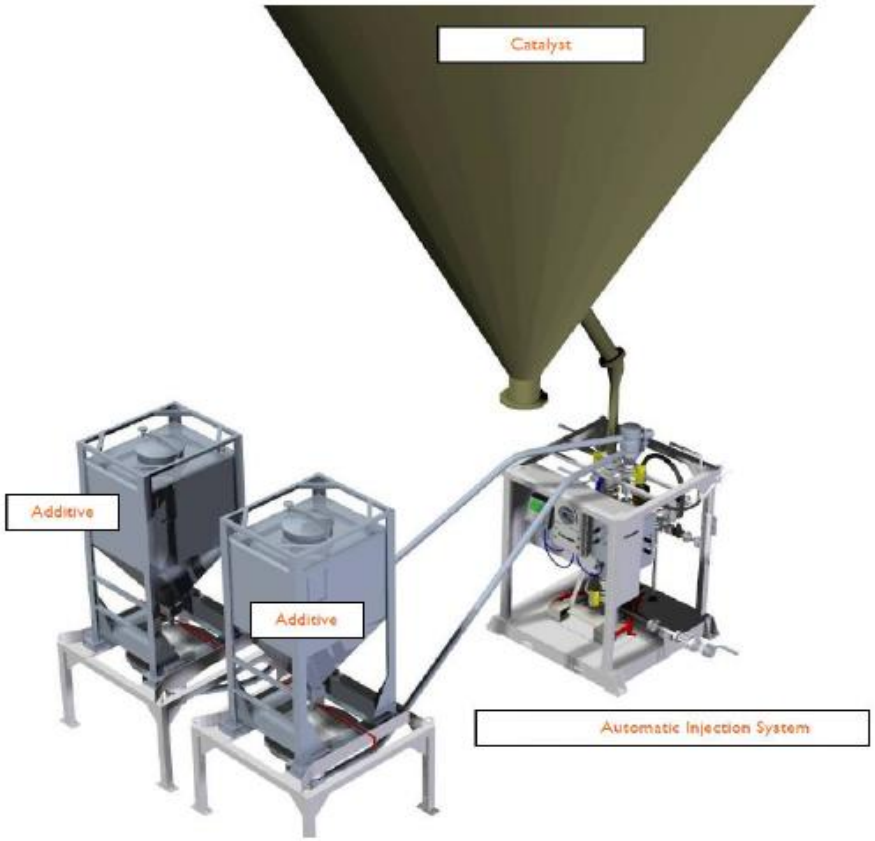
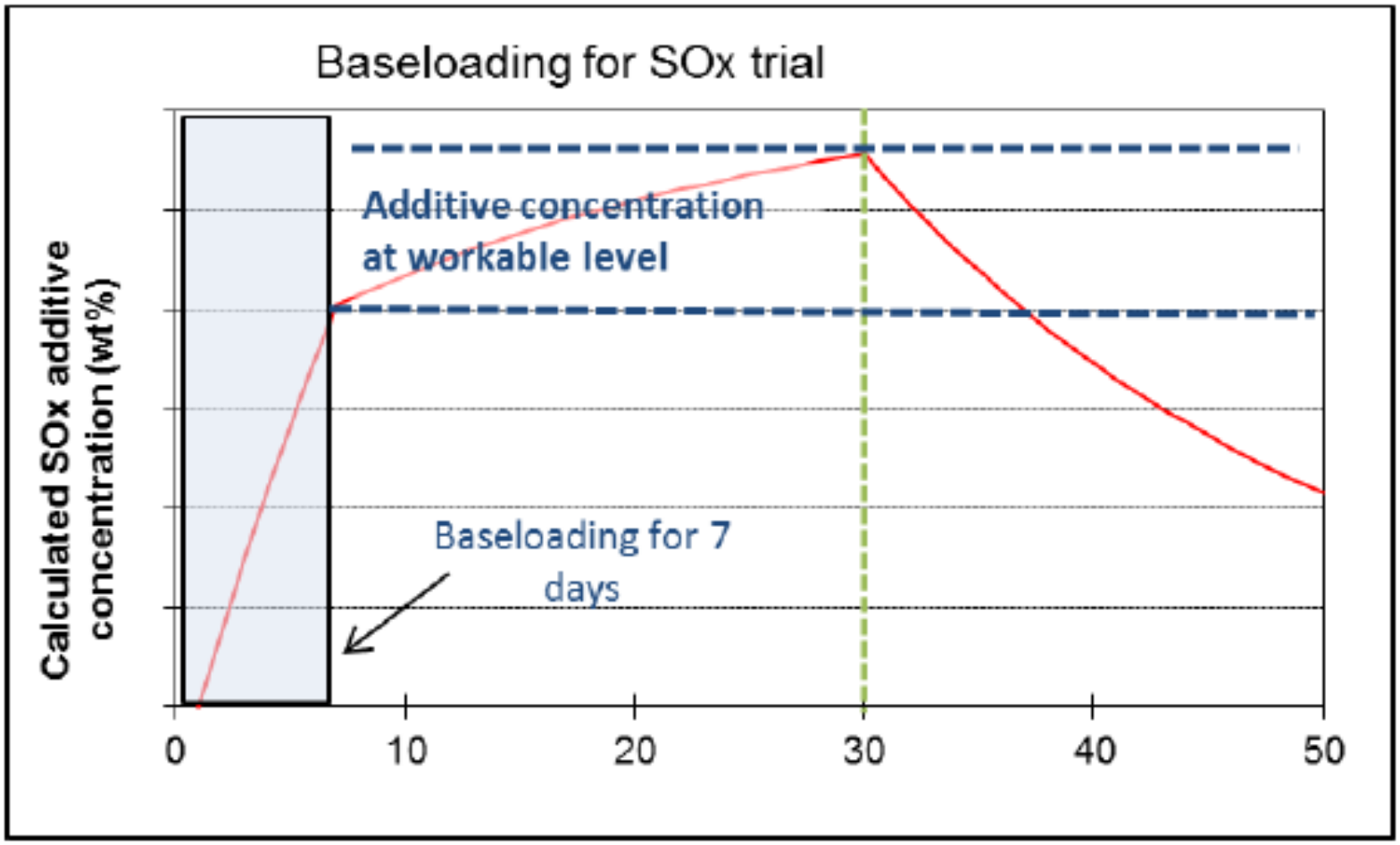


Figure by: Grace

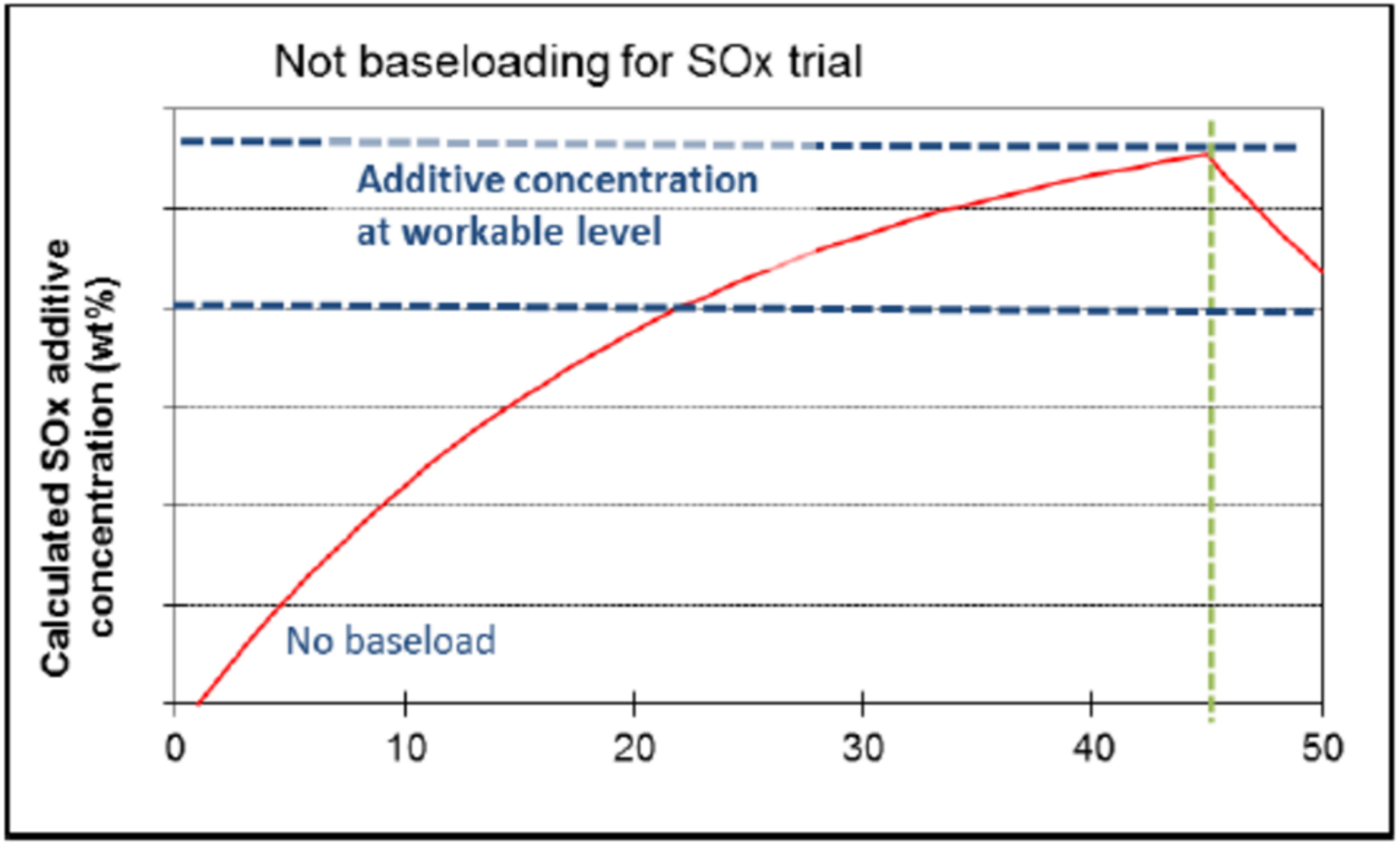
LOADING OF SOx ADDITIVES

FULL BURN UNITS

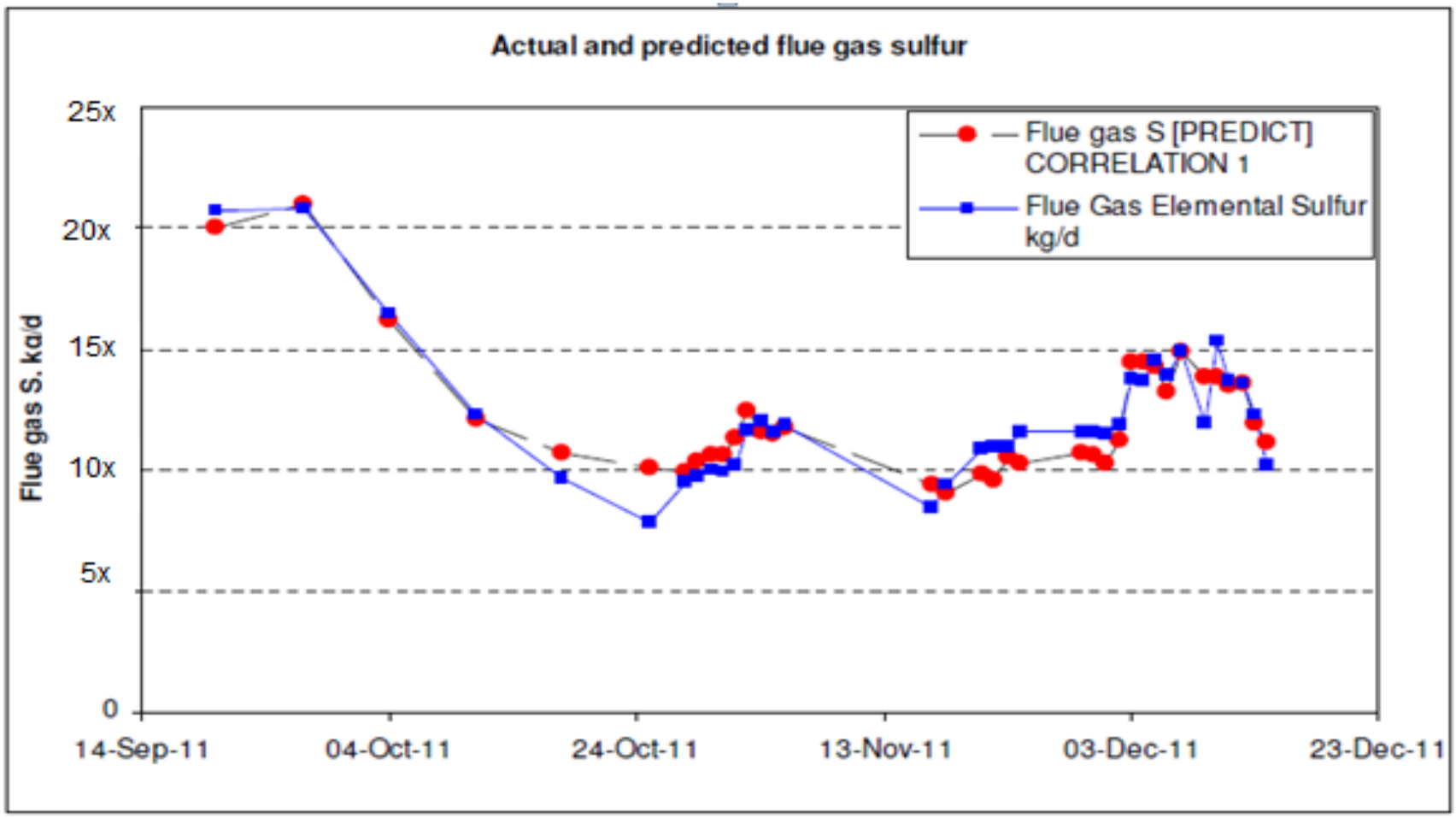


LOADING OF SOx ADDITIVES

PARTIAL BURN UNITS



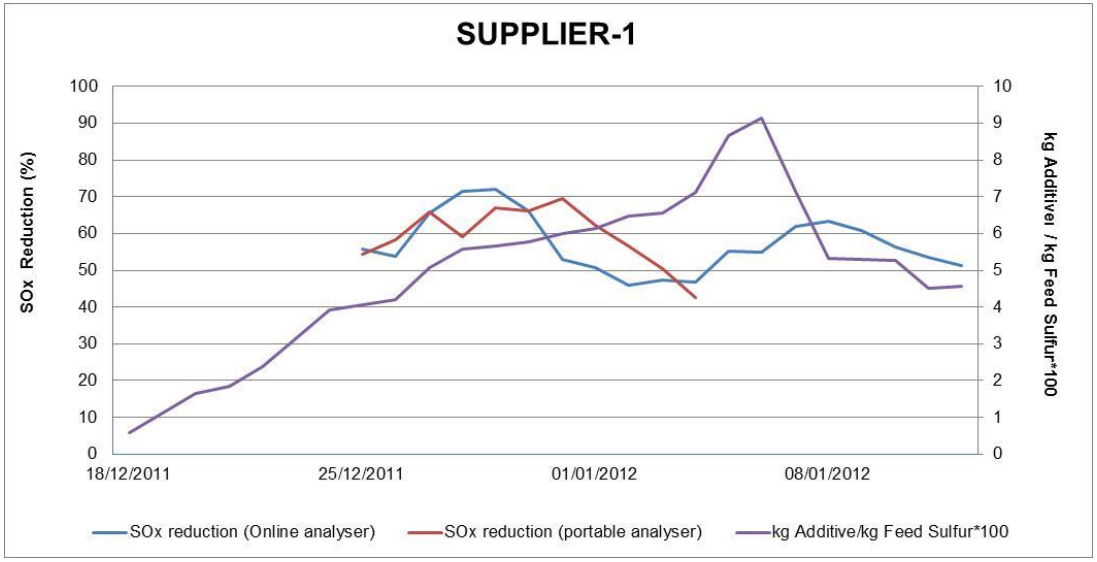
FLUE GAS SOx CORRELATION



Flue gas elemental sulfur (kg/day) = -14.241+0.107*Fresh Feed Elemental Sulfur Mass (kg/day)

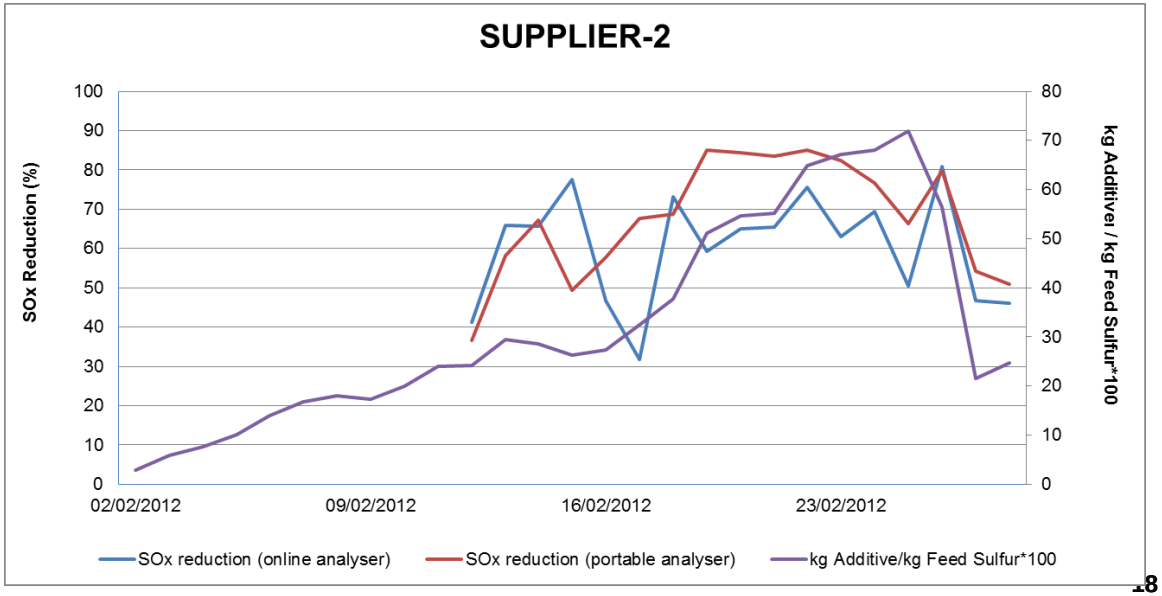
FG SOx (mg/Nm3) = Flue gas elemental sulfur (kg/day)/Air Rate (kNm3/h)/24*1000*2

FULL BURN TRIAL RESULTS

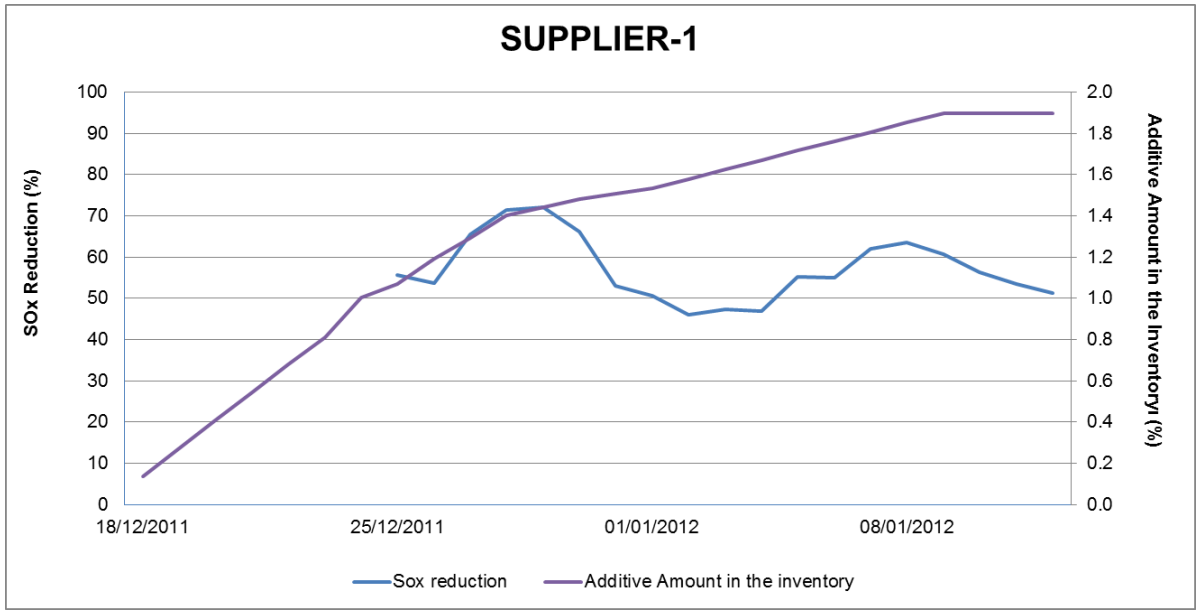


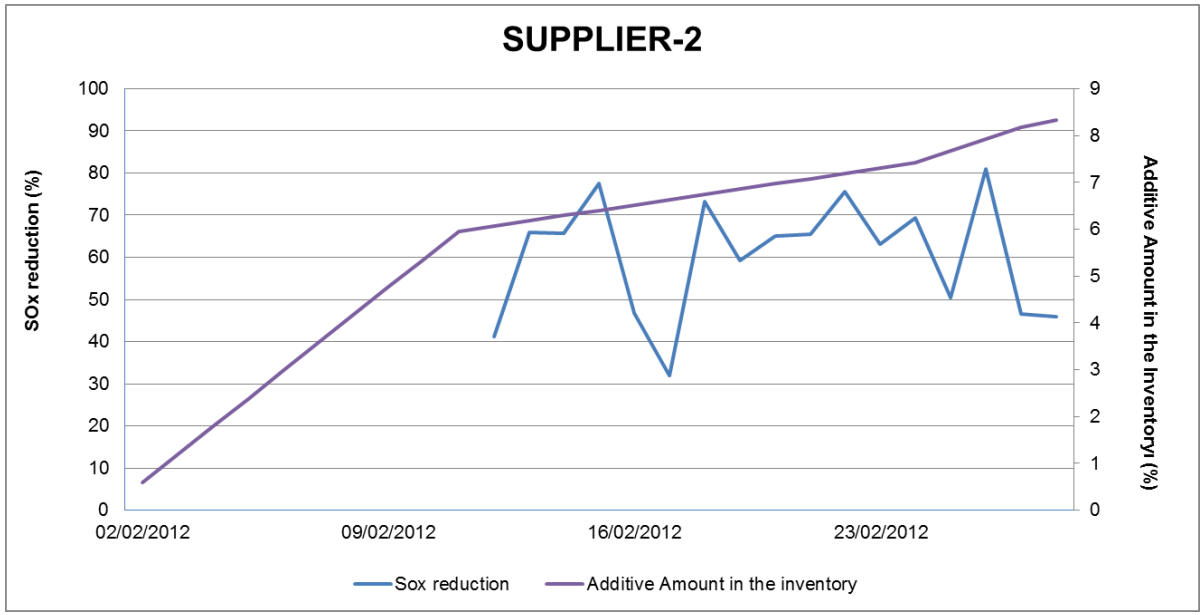
11 days of base loading at 100 kg/day, loading rate decreased to 40 kg/day after the base loading

10 days of base loading at 500 kg/day, loading rate decreased to 95 kg/day after the base loading



FULL BURN TRIAL RESULTS





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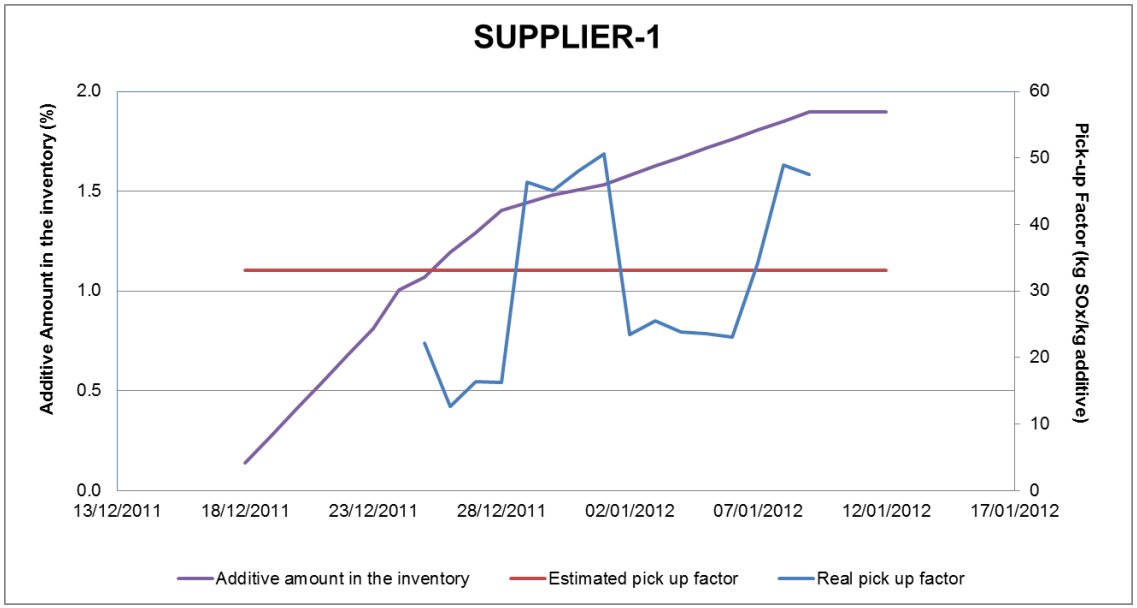
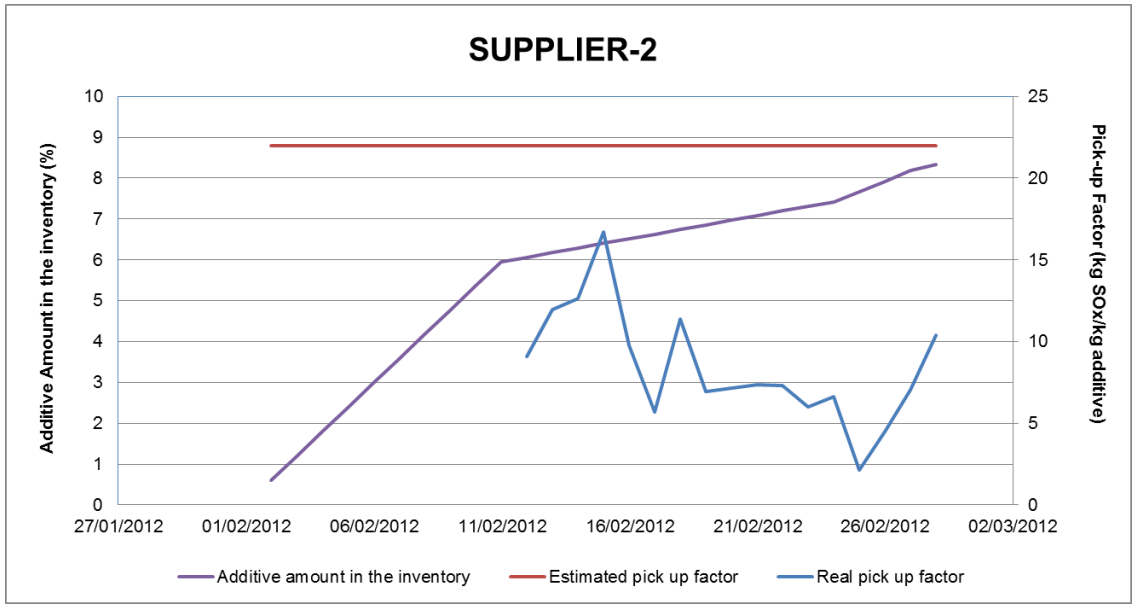
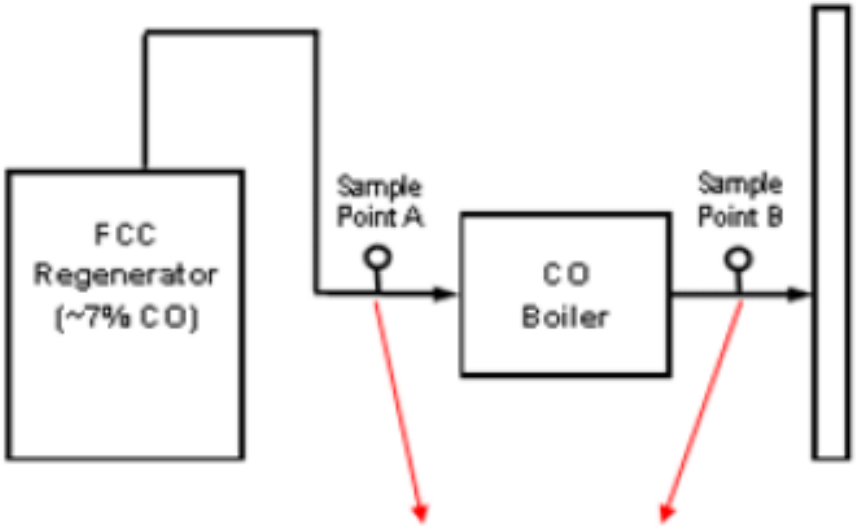




SOx VARIATION IN PARTIAL BURN UNITS

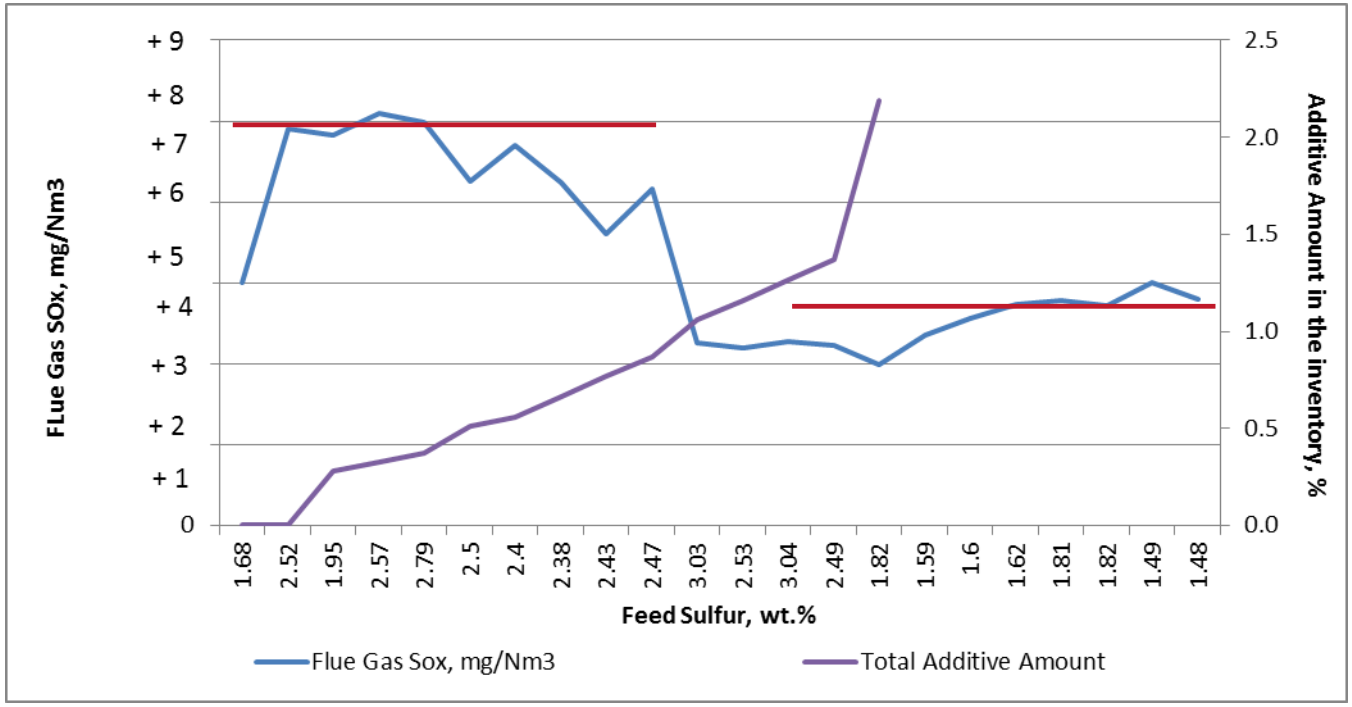


Flue Gas Analysis (mol/h)	CO Boiler Inlet	CO Boiler Outlet	% S Difference
Total SOx	x	3.1 x	32%

SOx Reduction in Stack: (10-CO) / CO *100

Figure by: Intercat

PARTIAL BURN TRIAL RESULTS



CO: CO_2 ratio kept constant during the trial

12 days of loading at 45 kg/day to observe CO: CO_2 ratio, loading rate increased to 100 kg/day after the base loading

50 -60 % reduction in SOx emissions

IMPORTANT POINTS IN ADDITIVE SELECTION

- Low consumption rates,
- High PUF,
- High SOx reduction,
- Effectiveness in short duration,
- Interaction with the catalyst,
- Low percentage in the inventory to aid the use of other additives without sacrificing from the general yield structure

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