Preventing the Most Common Environmental Excursions on the FCC

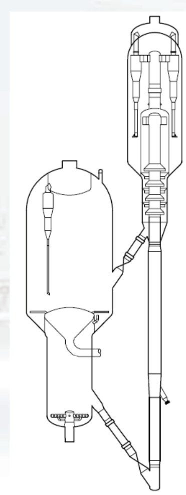
Ray Fletcher & Martin Evans

CatCracking.com

INTERCAT

Introduction

- **Refiners historically focus most attention on the reactor, riser & fractionation sections of the FCC**
- **Focus only applied to the regenerator when necessary due to catalyst losses, afterburn or when environmental regulations required**
- **With increasing environmental regulation, paying careful attention to the regenerator is key to avoiding unexpected emissions excursions**
  - The most common causes of SOx, NOx & CO emissions are provided
  - Regenerator optimization guidelines are included



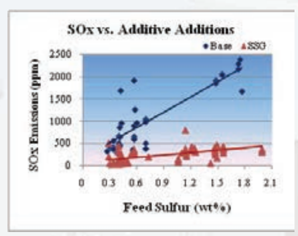
INTERCAT

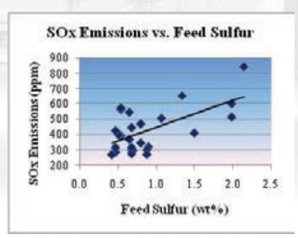
Overview

- **SOx emissions**
  - Feed sulfur & feed source variation, equilibrium Fe step changes, max LCO operations, loader failure, analyzer failure, excess oxygen, maldistribution, catalyst circulation & CO promoters
- **NOx Emissions**
  - Excess oxygen, CO-to-CO2 ratio, maldistribution, antimony & platinum
- **CO Emissions**
  - Start-ups, maldistribution, low CCR & deeply hydrotreated feeds
- **Conclusion**

SOx Emissions Control

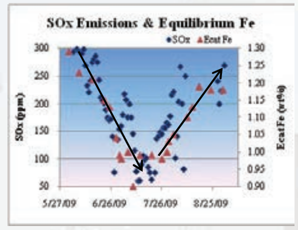
- **SOx additives effectively control SOx emissions from the FCC**
  - SOx additives most effective in full burn
  - SOx removal is directly proportional to additive addition rate
    - *Amount of removal only dependent on usage rate*
    - *Steady state emissions of < 5 ppm achievable*
- **SOx emissions will correlate with feed sulfur in some units**
  - More commonly correlate better with slurry S
    - *Coke S = UF*(slurry S)*$^{1.265}$
- **Most units process a limited number of feeds**
- **Amount of feed sulfur going to coke varies with feed stock**
  - *Regression techniques allow determination of feeds with greatest impact on emissions*



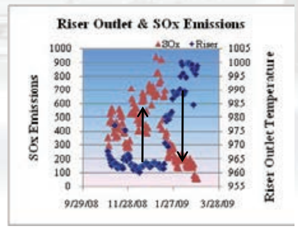


SOx Emissions Control

- **Feed iron excursions can have significant impact**
  - Effect on emissions may be large
  - Half life appears to be short
    - *Typically 2-3 days*
  - Increasing SOx additive rate sufficient control
  - Identify feed source



- **Maximum LCO mode operations**
  - Max diesel mode typically includes a reduction in riser outlet & stripper temperatures
  - May lead to insufficient additive regeneration
  - Intercat has developed additive technology effective in LCO mode operations

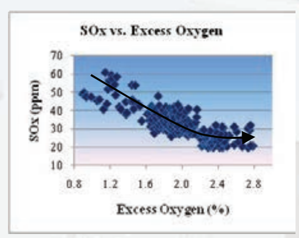


Riser outlet < 965 increases emissions

INTERCAT

SOx Emissions Control

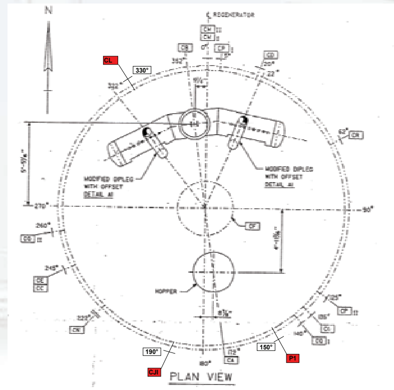
- **Additive loader failure**
  - Select loader supplier based upon highest equipment reliability
  - Loader should be capable of manual additions in case of power outage
- **Flue gas analyzer failure**
  - Regular maintenance required
  - Flue gas conditioning systems most common cause of poor readings
    - *Condensate removal*
    - *Catalyst fines removal*
- **SOx emissions are affected by excess oxygen**
  - Increasing oxygen leads to reduced emissions
  - Up to approximately 2% excess oxygen



INTERCAT

SOx Emissions Control

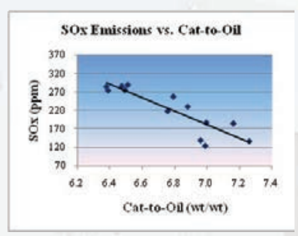
- **Regenerator maldistribution effects on SOx emissions**
  - Changes in air & catalyst distribution effect combustion efficiency
  - Maldistribution may result in oxygen rich & lean zones leading to increased SOx
  - Measurements taken with a Reaction Mix Sampling (RMS) device & a gas analyzer
  - Commercial example:
    - Full combustion regenerator
    - Northern half in partial combustion
    - Southern half in full combustion
    - Emissions differ according to oxygen concentration



	O2 (vol%)	CO (ppm)	SO2 (ppm)	Nox (ppm)
Position #1	0.1	2,828	440	152
Position #2	2.6	1,429	191	133
Position #3	4.3	1,068	83	218
Fluegas	2.6	83	248	109

SOx Emissions Control

- **SOx emissions affected by cat-to-oil**
  - CTO influences additive regeneration rate
  - Increased CTO results in increased regeneration and additive effectiveness
- **Platinum based promoters increase oxidation of SO_2 to SO_3 and thereby improve additive efficiency**



- **Guidelines for minimum SOx emissions:**
  1. Increase flue gas excess oxygen
  2. Lower regenerator temperature
  3. Increase regenerator pressure
  4. Increase catalyst circulation rate
  5. Use of platinum based CO promoter

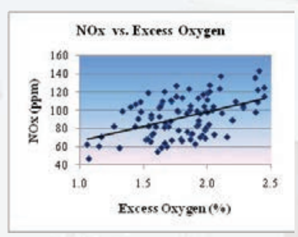
Overview

- **SOx emissions**
  - Feed sulfur & feed source variation, equilibrium Fe step changes, max LCO operations, loader failure, analyzer failure, excess oxygen, maldistribution, catalyst circulation & CO promoters
- **NOx Emissions**
  - Excess oxygen, CO-to-CO2 ratio, maldistribution, antimony & platinum
- **CO Emissions**
  - Start-ups, maldistribution, low CCR & deeply hydrotreated feeds
- **Conclusion**

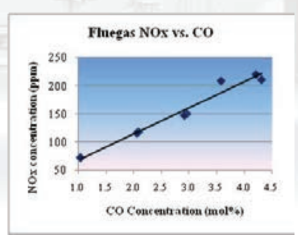
INTERCAT

NOx Emissions Control

- **NOx emissions strongly impacted by excess oxygen in full combustion**
  - Operate with the lowest stable excess oxygen level



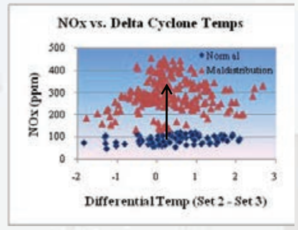
- **NOx emissions strongly impacted by CO concentration in partial burn**
  - Operate with lowest stable CO concentration



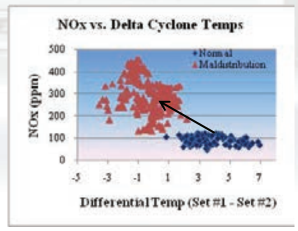
INTERCAT

NOx Emissions Control

- **NOx emissions strongly impacted by regenerator maldistribution**
  - Analysis techniques:
    - *Directly measure regenerator NOx levels with an RMS device & a portable gas analyzer*
    - *Plotting NOx emissions against delta cyclone outlet temperatures will indicate where maldistribution is occurring*
    - *Multi-variable linear regression of independent variables*
- **Antimony for Ni passivation increases NOx in many but not all units**
  - Verification of antimony effect recommended
  - Use Ni trapping catalysts where possible



Normal shift

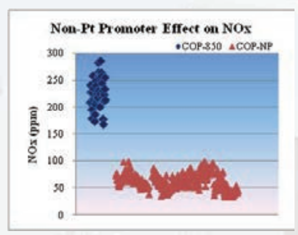


Abnormal Shift

INTERCAT

NOx Emissions Control

- **Platinum based CO promoters**
  - Platinum oxidizes nitrogen in coke to NOx
  - Non-platinum promoters effectively control afterburn with lower NOx
    - Typical reductions are 50-70%
    - Beware of over-promotion
- **Unit optimization for reduced NOx emissions**
  1. Operate a full combustion regenerator at minimum excess oxygen
  2. Operate a partial burn regenerator at minimum CO-to-CO_2 ratio
  3. Avoid platinum based promoters
  4. Carefully monitor antimony injections
  5. Use a non-platinum based promoter for after burn control or a NOx additive



"One refiner having switched to a non-Pt promoter later "found" a bin of Pt-based promoter in the warehouse, delivered it to the unit, began injections, and went out of compliance. Learning point: ensure no Pt-based promoter is in stock after switching to a non-Pt promoter!"

INTERCAT

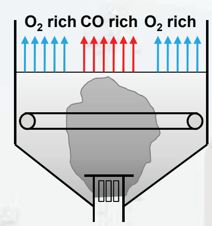
Overview

- **SOx emissions**
  - Feed sulfur & feed source variation, equilibrium Fe step changes, max LCO operations, loader failure, analyzer failure, excess oxygen, maldistribution, catalyst circulation & CO promoters
- **NOx Emissions**
  - Excess oxygen, CO-to-CO2 ratio, maldistribution, antimony & platinum
- **CO Emissions**
  - Start-ups, maldistribution, low CCR & deeply hydrotreated feeds
- **Conclusion**

INTERCAT

CO Emissions Control

- **This analysis focuses on the full combustion regenerator**
  - Most well designed CO boilers will easily control CO emissions
- **FCC start-ups are the most common cause of CO emissions**
  - Slugs of oil soaked catalyst entering the regenerator may result in a temporary partial burn mode
  - Many operators will add a CO promoter during start-up as a precaution



Source: J.W. Wilson, AM-03-44

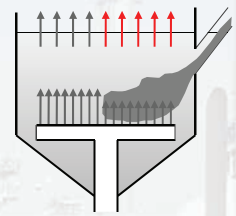
Flue gas CO survey

Date	Time	CO	SO_2	NOx
Day 1	1110	7	71	35
	1112	79	69	39
	1355	396	85	52
	1401	12	60	57
Day 2	0824	4	83	40
	0831	5	97	35
	1030	2	105	35
	13:30	1	91	45

INTERCAT

CO Emissions Control

- **Maldistribution**
  - Maldistribution due to mechanical damage or design flaws will result in increased CO production
  - Poor air & catalyst distribution will result in oxygen and CO rich zones leading to afterburn and possibly CO emissions
  - CO promoters are effective at controlling CO emissions



Source: J.W. Wilson, AM-03-44

- **Clean feeds**
  - Operating low CCR or deeply hydrotreated feedstocks at low regenerator bed temperatures may result CO break through
  - Control responses:
    - Increase bed height & temperature if possible
    - Add CO promoter

INTERCAT

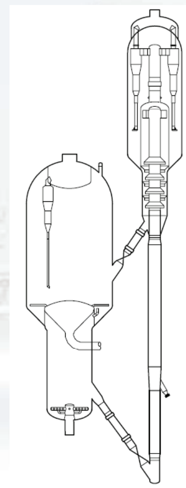
Overview

- **SOx emissions**
  - Feed sulfur & feed source variation, equilibrium Fe step changes, max LCO operations, loader failure, analyzer failure, excess oxygen, maldistribution, catalyst circulation & CO promoters
- **NOx Emissions**
  - Excess oxygen, CO-to-CO2 ratio, maldistribution, antimony & platinum
- **CO Emissions**
  - Start-ups, maldistribution, low CCR & deeply hydrotreated feeds
- **Conclusion**

INTERCAT

Conclusions

- **Careful attention to the FCC regenerator will:**
  - Maximize combustion efficiency
  - Minimize the probability of unexpected flue gas emissions
- **The time commitment by the process engineer is minimal if these techniques are incorporated into daily monitoring routines**
- **Swift determination of the root cause of flue gas emissions should be enhanced using these techniques**



Ray Fletcher ~ rfletcher@intercatinc.com
Martin Evans ~ mevans@intercatinc.com