



Taking steps to reduce FCC NO_x emissions

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Temperatures in the fluid catalytic cracking (FCC) regenerator are insufficiently high to produce thermal NO_x from nitrogen in combustion air. However, in units with CO boilers that are typically found on partial burn FCC units (FCCUs), the introduction of direct firing will result in thermal nitrous oxides (NO_x) being produced downstream of the FCC regenerator. This is particularly true in cases where the CO boiler has not been fitted with low- NO_x burners.

Feed nitrogen that has been converted to coke in the reaction section can leave the process as NO_x in the flue gases when said coke is combusted in the regenerator. Approximately 40% of feed nitrogen will partition into coke. Nitrogen in coke will not automatically fully convert to NO_x . Many different reaction paths exist. 75% of nitrogen in coke is converted to inert nitrogen (N_2), which leaves as a harmless inert. The remaining 25% will be converted to NO_x (NO , NO_2 , N_2O) or a reduced nitrogen species, such as hydrogen cyanide (HCN) or ammonia (NH_3). Reduced species will tend to form when available free oxygen is sparse; this is strongly the case in partial burn FCC regenerators and some full burn regenerators where radial mixing between spent catalyst and air is non-uniform. Reduced nitrogen species are readily converted to NO_x when they come into contact with oxygen, either in more oxygen-rich sections of the catalyst bed or vapour space, plenum, flue gas ducting or in the presence of excess air injected into the CO boiler.

Oxygen is a key factor in determining if nitrogen in coke forms N_2 or NO_x in the FCC regenerator. A surfeit of oxygen will push the reaction further in the direction of NO_x rather than N_2 in the oxygen rich environment of the downstream CO boiler. Similarly, a lack of oxygen will increase the formation of reduced nitrogen species, which terminates as NO_x rather than N_2 . The theoretical 'sweet spot' of oxygen would be the point between full burn and partial burn, i.e. close to zero excess O_2 and ppm levels of CO in the flue gas. Although it is not a feasible regime to operate an FCC regenerator in a stable manner, combustor-type units and counter-current regenerators aim to be close to this sweet spot in key areas of the regenerator. Hence, these units tend to have lower levels of NO_x emissions from the outset. There may be separate drawbacks to this type of regenerator design in terms of other environmental emissions, but this discussion is not in the scope of this article.

In partial burn units, a higher CO/CO_2 ratio implies more reductive atmosphere, which pushes nitrogen in coke through pathways leading to reduced N-species, such as HCN and NH_3 . These reduced species become fully oxidised to NO_x with surplus oxygen in the CO boiler.

Platinum (Pt) complexes that are present in CO promoters and antimony are strong catalysts in the generation of NO_x from nitrogen in coke. Although it is plausible that the presence of CO can act to reduce NO_x to N₂ ($2\text{CO} + 2\text{NO} \rightarrow 2\text{CO}_2 + \text{N}_2$), this may be very localised and heavily outweighed by the aforementioned significant generators of NO_x.

CO promoters are used in FCCUs, more commonly in full burn than partial burn operations, to reduce afterburn. 'Afterburn' is defined as the positive temperature delta between the dilute phase of the regenerator and dense bed phase. This difference forms as a result of excess CO slipping from the dense bed, meeting an excess of O₂ in the upper regenerator and fully oxidising through to CO₂. The CO oxidation reaction is highly exothermic and the low density or heat capacity of the vapour space limits how much of this heat of combustion can be absorbed. Traditionally using platinum as the active material, CO promoters catalyse this final oxidation reaction within the dense bed, where the temperature is more effectively buffered by the surrounding catalyst.

CO promoters can be poisoned by lead and antimony. Lead (Pb) can irreversibly poison platinum CO promoters at a ratio of 100:1 Pb/Pt. Promotion activity may be reduced by 50% when using antimony. The amount of CO promoter required for a given operation to maintain effective afterburn control is conventionally termed 'the level of promotion'. A fully-promoted system is when the amount of CO promoter in use results in 2 ppm of platinum present in the total circulating inventory at steady state. Units that find it challenging to maintain control of afterburn can increase this level. Other units may be able to achieve good control with less than 1 ppm of platinum.



Optimisation of the FCC

The push to minimise CO promotor use is prudent. Not only does it save on OPEX as precious metal containing additives are naturally expensive, but NO_x emissions can be reduced significantly by limiting the amount of platinum or palladium added to the FCCU.

The first action to take is optimising the operation to minimise excess O₂ in full burn applications and reducing the CO percentage in partial burn applications. The next step for decreasing FCC NO_x emissions is adding the CO promotor separately rather than pre-blending it with the catalyst. If the CO promotor is pre-blended with the catalyst, the control available to the operator to carefully optimise actual CO promotor requirement is made redundant. There is also concern if the CO promotor is truly ideally mixed with the catalyst and if the fresh catalyst addition system can add batches of catalyst in the accurate and semi-continuous way for the required application. With these factors acting against the pre-blended approach, progressive refiners often realise that separate addition with a reliable and accurate addition system is critical for reduced NO_x emissions.

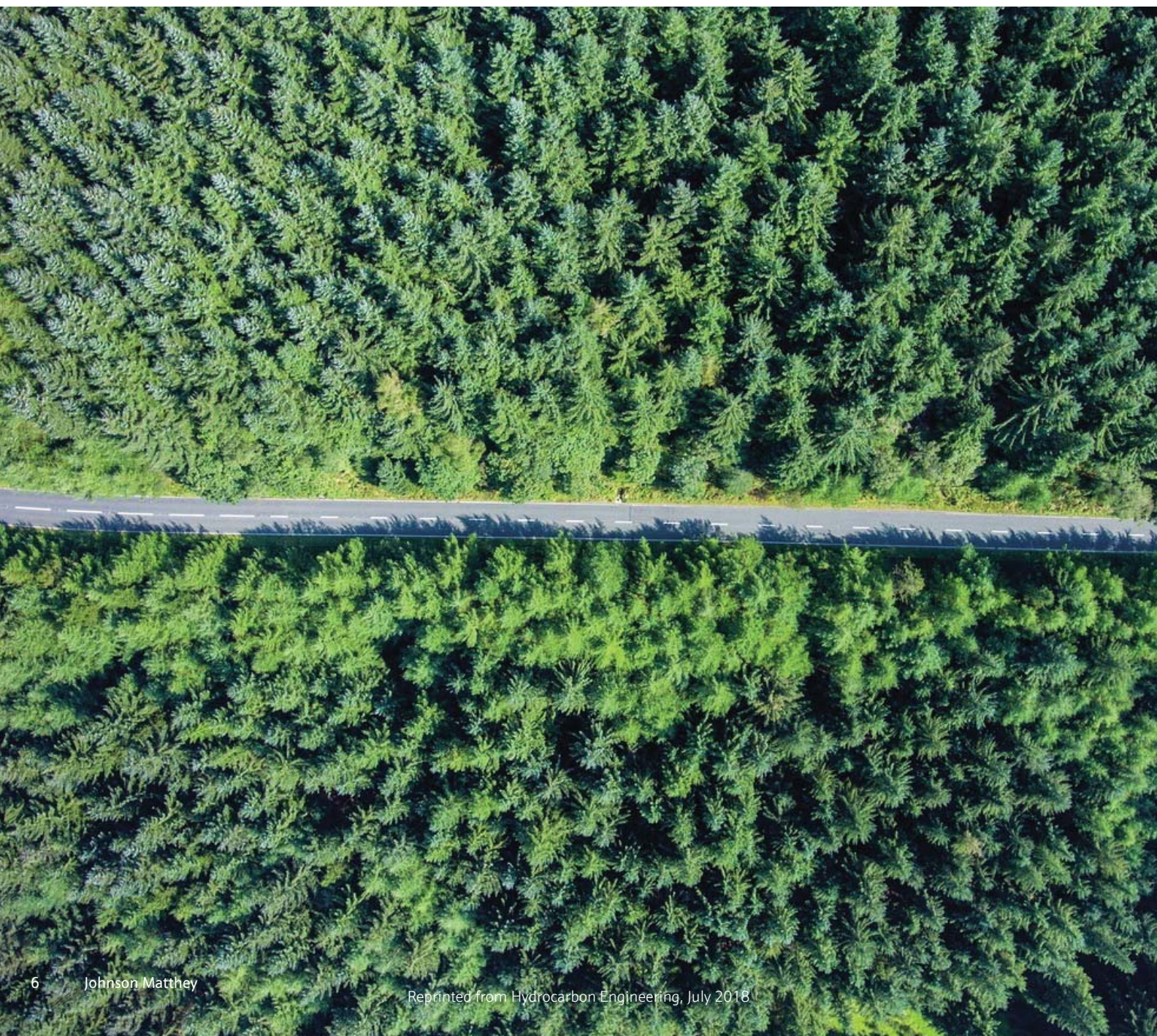
Refiners that pre-blend will find that CO promotor addition rate is set conservatively in an effort to overcome the issues during unstable operation. Moreover, transient high afterburn events can occur, particularly during a start-up,

resulting in the need to inject additional promotor for a short period of time. If promotor is wholly pre-blended and there is no capability to add extra material, the pre-blend level may even be set for this worst-case/start-up operation, resulting in an over-addition of promotor in the vast majority of the operation.

Constantly changing the proportion of promotor included in the pre-blend catalyst is also unfeasible. Firstly, there is little way of checking the accuracy of this variable concentration due to the inability to accurately measure low levels of Pt. Also, the long-decay period of platinum in the catalysis of NO_x and the short-decay period for CO promotion reactions means that targeting continuous optimal operation in a dynamic unit, such as the FCC, is almost impossible, especially when catalyst hopper turnover and delivery times extend the lead time that needs to be taken into account.

NO_x reduction in full burn FCC

Following the optimisation of the FCC operation, the separation of CO promoter addition and the optimisation of promoter addition rate for stable afterburn control, the refiner may find that this improvement process has given an adequate reduction in NO_x emissions to satisfy the environmental limits required. If this is not the case, the next step of switching to an effective non-platinum based CO promoter is typically sufficient to meet NO_x reduction requirements for most European FCCUs – giving a reduction in NO_x of up to 70%. In the unlikely event that further NO_x reduction is required, specific NO_x additives may also be used in certain FCCUs that show a sensitivity.



If the implementation of all the above steps does not give the required NO_x reduction to achieve current or impending European regulations, it is likely that the design of the regenerator or mechanical failure in the regenerator is leading to elevated NO_x emissions. In such a case, online improvements may not yield the reductions required and a radical redesign or maintenance shutdown will be necessary.

Alternatively, there are several end-of-pipe solutions that can be used in units with extreme NO_x issues or partial burn units that are not able to take advantage of changes in CO promoter type (although partial burn units that use CO promoter can still benefit from switching to an effective non-platinum promoter). Selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR) are among these technologies.

In SNCR, NH_3 or urea nozzles are installed in the convection section of CO boilers. These nozzles are used to atomise NH_3 at temperatures of 850 – 1030°C. NH_3 will react with NO_x species through to N_2 . NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ salts can form as byproducts, causing plugging and corrosion downstream. NH_3 slip can reach as high as 20 ppm in the stack gas in an SNCR process, depending on the quality of NH_3 :NO ratio control in the reaction section.

In the SCR process, a V_2O_5 or WO_3 based catalyst aids the formation of N_2 from NO_x , using air and NH_3 as reactants. Optimum operational temperature is between 300 – 400°C and the catalyst life is typically between four to six years. The catalyst is mounted in a CO boiler or separate vessel. Salts can also cause plugging of the catalyst in this process.

NO_x can be decreased by 40 – 75% by the SNCR process and 70 – 90% by the SCR process. In wet gas scrubbers, NO_x is converted to N_2O_5 and then to HNO_3 by ozone. Nitrogen leaves the process as NaNO_3 through reaction with NaOH . NO_x removal is above 98% by WGS, but this is highly costly in terms of initial investment and operating cost. In addition, treatment of NaNO_3 and NaSO_4 enriched steams is typically required. Otherwise, crystallisation units are required to remove salts from the purge streams, resulting in further capital and operational costs.

Case study

Tüpras investigated NO_x mitigation methods when challenged on this subject in 2011. The following section details the company's experience when implementing its chosen technologies.

Tüpras Izmit Refinery has an FCCU that is designed for a feed rate of 1750 m³/d of HVGO/HCO/naphtha recycle. The unit is a UOP side-by-side configuration with a bubbling bed regenerator operating in full burn, a riser disengaging system with rough cut cyclones and feed injection at the bottom of the riser. The unit's current operating capacity is 2250 m³/d.

The refinery began using Johnson Matthey's non-platinum **COP-NP**TM CO promoter in April 2013, replacing a traditional platinum-based CO promoter that was pre-blended with the FCC fresh catalyst to a level of 2 ppm platinum. A later trial of the company's **NOXGETTER**TM additive began in November 2013. An addition rate of 3 kg/d of **COP-NP** was required for this unit with 80 t of circulating catalyst inventory.

After the CO promoter switch, any platinum remaining in the inventory will continue to generate NO_x long after the CO promotion capabilities have diminished. Therefore, Tüpras calculated a platinum decay profile based on a CSTR model (Figure 1). Based on this calculation, it takes more than 200 days to decrease platinum to a level below 1 ppm. There was a further interruption to the normal decay when catalyst pre-blended with platinum had to

be loaded to the inventory in June 2013. This introduced a small deviation in inventory platinum concentration. However, towards the end of the period and by the start of the additive trial in November 2013, the platinum concentration had fallen to a low background level. The platinum decay profile approximates the turnover of the unit as a function of daily addition and withdrawal rates and the catalyst inventory of the system. Therefore, the fall in NO_x at Tüpras Izmit Refinery followed the platinum decay curve after changing to non-platinum CO promoter (Figure 2).

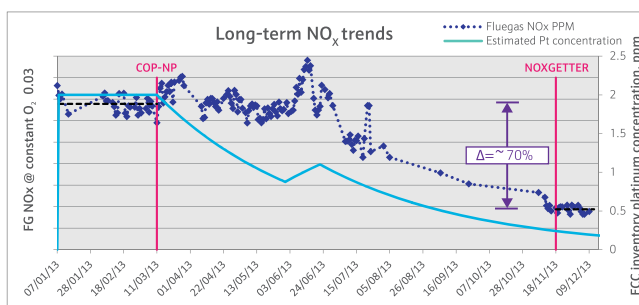


Figure 2. NO_x emissions during reduction trials.

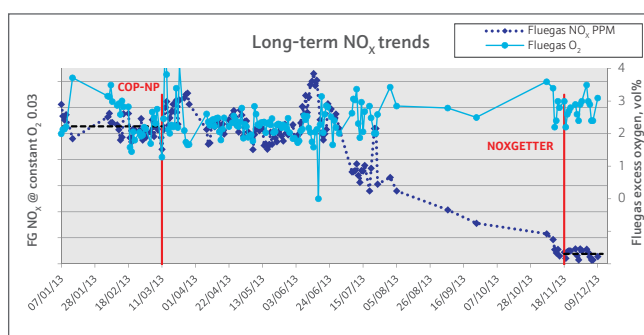


Figure 3. The relationship between NO_x emissions at excess O₂ in the refinery's FCCU.

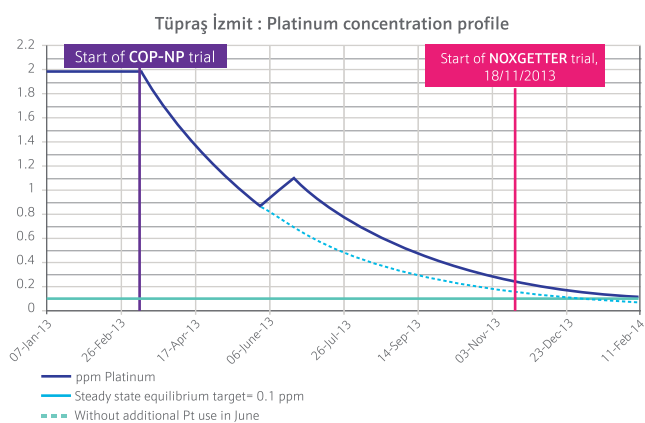


Figure 1. Platinum decay during NO_x reduction trials at Tüpraş Izmit Refinery.

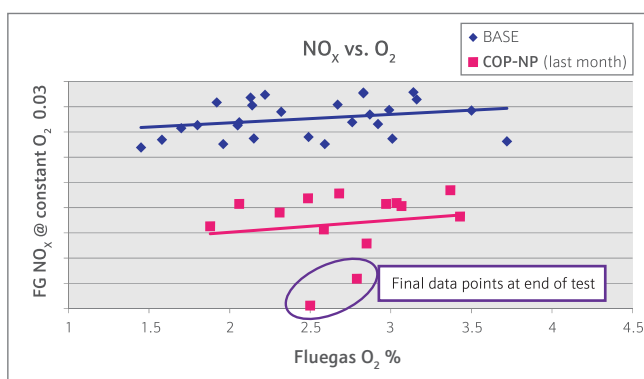


Figure 4. NO_x vs excess O₂, focusing on operation with **COP-NP** when platinum concentration has decayed to a low level.

While it is generally expected that NO_x emissions will follow the platinum decay curve, moving from 2 ppm to 1 ppm platinum concentration is still a large amount of platinum present in the inventory. Moreover, despite being aged, it is still highly active in producing NO_x . After the platinum-containing batch of catalyst had been consumed in June 2013, NO_x began to decay with the platinum concentration. The platinum concentration also reduces below 1 ppm for a sustained period at this point (Figure 3).

At fixed excess O_2 , Johnson Matthey's CO promoter was found to reduce NO_x emissions by 32% in the latter part of the test when platinum in Ecat has decayed to a lower level. However, it appeared that NO_x emissions were continuing to decrease in line with further reductions in platinum concentration. Based on the final days of operation before the start of the next trial, NO_x could be concluded to be 54% lower than the baseline. This is more in line with NO_x reduction levels of ~60% that are expected when switching to an effective non-platinum CO promoter (Figure 4).

An important differentiator for Tüpras when exploring low- NO_x CO promoters was the ability to maintain good afterburn control with a reduced amount of platinum or platinum alternative. Commercial data showed that **COP-NP** can provide effective afterburn control without the use of platinum. During the Izmit testing, no discernible difference in afterburn was observed when switching from platinum CO promoter to the replacement non-platinum CO promoter (Figures 5 and 6).

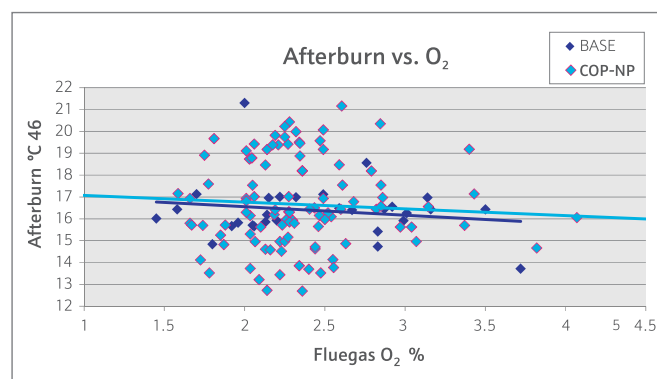


Figure 5. Cross-plot of afterburn vs excess O_2 .

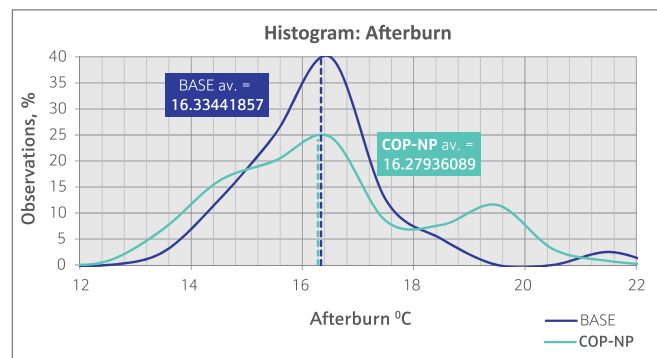


Figure 6. Daily average afterburn in the base period using 2 ppm platinum-based CO promoter in fresh catalyst and Johnson Matthey non-platinum promoter.

To determine the potential for further reductions in NO_x in the Izmit FCCU, a trial of separate NO_x reduction additive was performed.

The trial strategy was to perform additions to attain 1% concentration in the FCC inventory and then towards 2%. Steady-state concentration was not achieved but over the course of this 25-day trial enough useful data was collected to analyse the additive effects (Figure 7).

Up to the start of the additive trial, further declines in the residual platinum concentration in the FCC inventory appeared to still dominate NO_x generation. The additive proved to reduce a further 31% NO_x emissions at constant Ecatt platinum concentration (Figure 8).

The comparison at constant excess O_2 is not as strongly correlated but still indicates significant NO_x reduction with **NOXGETTER**, independent of the main driver of FCC NO_x generation observed in full burn FCCUs (Figure 9).

Based on previous experience, it is not anticipated that feed nitrogen has a significant effect on FCC NO_x generation. This is because the sensitivity of NO_x emissions is primarily located in the regenerator in terms of the skew of reaction pathways to either N_2 or NO_x . Therefore, throughout the Tüpras Izmit NO_x trials, no sensitivity with feed nitrogen was observed. Also, feed nitrogen was maintained in a similar range of 600 – 1200 ppm through the entirety of the base case and trial periods (Figure 10).

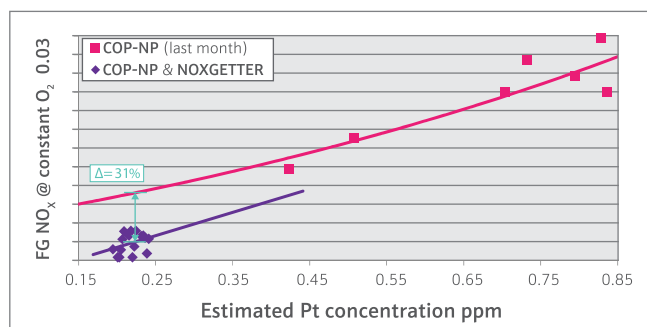


Figure 8. NO_x vs Ecatt platinum concentration through the additive trial.

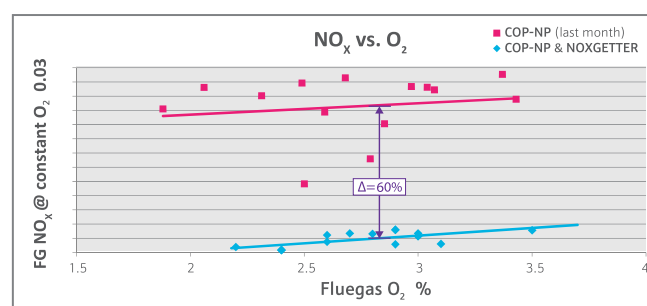


Figure 9. NO_x vs excess O_2 during the additive trial.

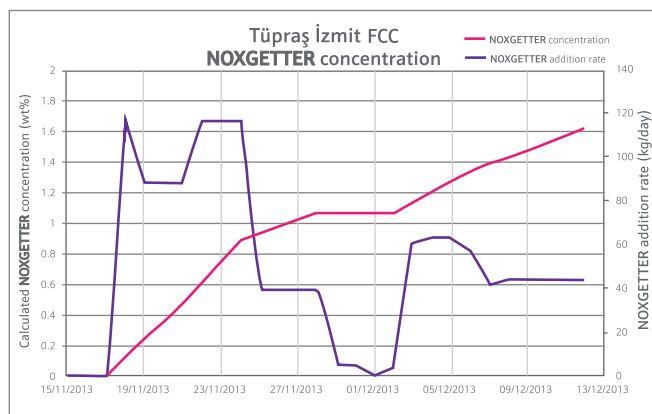


Figure 7. **NOXGETTER** addition protocol through the trial phase.

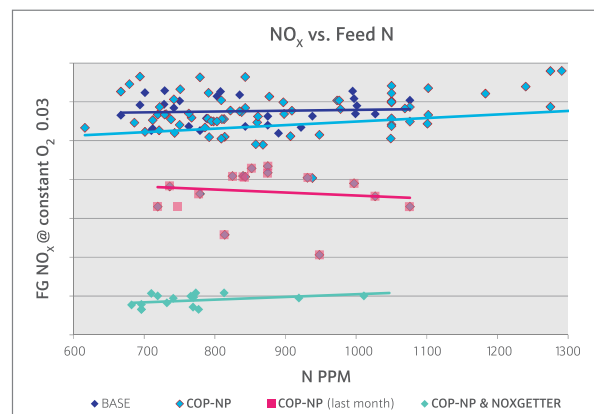


Figure 10. NO_x vs feed nitrogen during the NO_x analysis period at the refinery.

Conclusion

Working alongside Johnson Matthey, Tüpras embarked on a comprehensive study of the possibilities for reducing NO_x emissions from the Izmit FCCU. A NO_x reduction of almost 75% was realised and a stepwise procedure was followed to achieve this reduction. A significant reduction in NO_x was observed when switching to a separately added platinum-free CO promoter that is effective in afterburn control. This helped reduce NO_x by almost 60%. A subsequent trial with an additive used reduced NO_x to the point that the overall reduction was 74% on a constant excess O_2 basis (Figure 11).

Feasibility studies of this kind can help companies approach current and future changes to environmental emission standards, following learning derived from the performance of short but rigorous plant trials.

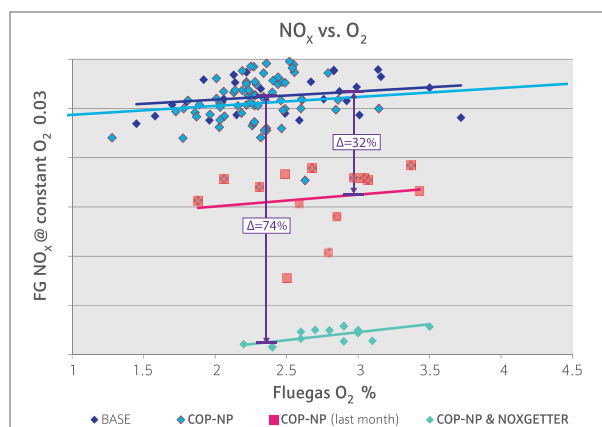


Figure 11. NO_x vs excess O_2 over the whole NO_x reduction period.

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