



## Full Length Article

## Selective non-catalytic reduction – Fe-based additive hybrid technology



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## HIGHLIGHTS

- A Fe-based additive altered performance of selective non-catalytic reduction.
- Pseudo-catalytic activity provides active sites for ammonia to reduce NO.
- This interaction led to greater NO reduction and greater ammonia utilisation.
- This is an economically viable opportunity for full-scale coal combustion plants.

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## ABSTRACT

Fe-based additives can be used to improve coal combustion and reduce NO<sub>x</sub> emissions; further to this, iron oxide (Fe<sub>2</sub>O<sub>3</sub>) has been found to interact with ammonia. Therefore, it is critically imperative to understand and assess the impact of the Fe-based additive on the use of ammonia based selective non-catalytic reduction (SNCR) and to evaluate the economic feasibility of such a combination for full-scale use. Experiments were performed using a 100 kWth down fired-combustion test facility burning pulverised coal over three Fe-based additive concentrations, while the ammonia input was varied between normalised stoichiometric ratios 0–3. This study finds evidence of an interaction between the Fe-based additive and SNCR. The interaction leads to greater ammonia utilisation and an increased NO<sub>x</sub> reduction due to the SNCR of >10%. The interaction is theorised to be pseudo-catalytic with the fuel additive providing an active site for ammonia to reduce NO. Using Carnegie Mellon University's 'Integrated Environmental Control Model' (IECM), this has been shown to create an economically viable opportunity to increase SNCR effectiveness.

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## 1. Introduction

The use of coal for power generation has only grown in popularity across the world in spite of leading nations pledging to maximise efforts to reduce the inevitable impact of climate change, in solidarity with many other future affected nations. The focus of many energy researchers is therefore to create opportunities for economical clean coal technologies, particularly regarding innovative SO<sub>x</sub> and NO<sub>x</sub> control technologies.

NO<sub>x</sub> abatement technologies have been extensively reviewed [1] and are understood to be largely split into two categories: combustion modification and post combustion abatement. The most common combustion modification techniques include variations of low NO<sub>x</sub> burners and over fire air (OFA); these can have the

unintended side-effect of reducing the combustion efficiency and increasing carbon in ash [2]. Nevertheless, they are a popular choice when a European plant operator is in need of economical NO<sub>x</sub> reduction; this is due to only modest costs [2] and their ability to reach the old Large Combustion Plant Directive (LCPD) (2001/20/EC) [3] emission limits. Under the Industrial Emissions Directive (IED) (2010/75/EU), existing coal and biomass plants over 500MW<sub>th</sub> and new coal and biomass plants over 300MW<sub>th</sub> in the EU are required to keep their NO<sub>x</sub> emissions below 200 mg/Nm<sup>3</sup> [4]. In the UK, this has been a costly and laborious task, and has already seen a number of coal power plants opt-out and choose to shut down [5]. In China and the US, these limits are even tighter reaching 100 mg/Nm<sup>3</sup> [6] and 117 mg/Nm<sup>3</sup> [7] respectively. These emission limits effectively require plant operators to install a post-combustion abatement technology; this has forced a dilemma: accept the large financial blow but secure long-term NO<sub>x</sub> compliance with selective catalytic reduction (SCR) or install selective non-catalytic reduction (SNCR) at a low cost and risk intermittent limit breaches. This is a simpler choice for those running on bio-

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### Nomenclature

AFR	ammonia flow rate (ml/min)	NSR	normalised stoichiometric ratio
$\eta_{\text{NH}_3}$	ammonia utilisation efficiency	Q	volumetric flow rate of air (ml/min)
$\text{NO}_{\text{initial}}$	the concentration of NO in the flue gas prior to ammonia injection (ppm)		

mass, or co-firing with biomass, as initial NO concentrations tend to be far lower.

SCR can achieve NO<sub>x</sub> reductions of up to 90% [2], however the catalyst that makes this possible is prone to rapid fouling and the whole process is known to be very cost intensive (around \$2600–7400/ton of NO reduced [8]). SNCR is seen as a less attractive prospect with a substantially lower maximum removal rate (in this paper found to be ~45%); however, it is relatively simple to implement [2] and far less cost intensive (around \$670–2200/ton of NO reduced [8]) than SCR. SNCR is also attractive due to being unaffected by fly ash and easily modified to work with other NO<sub>x</sub> abatement technologies [9].

The technique of SNCR involves the reduction of NO by a reagent, usually ammonia or urea, at a temperature window between 850 °C and 1175 °C [2]. The reagent, ammonia in this study, reacts with hydroxyl radicals (OH) to form an amidogen radical (–NH<sub>2</sub>):



This radical is selectively reactive towards NO and primarily reacts in the following reactions:



Reaction (R3) is important because it is a chain branching reaction that regenerates OH radicals needed for the chain propagation reaction (R1). However, the NNH radical undergoes a further reaction:



Which leads to:



The H atom is then involved in a chain branching reaction to create more hydroxyl radicals. Therefore, even though reaction (R3) is not as efficient as reaction (R2) at reducing NO, it is just as vital because it leads to the SNCR process being self-sustaining.

Another option would be to install SNCR while also capitalising on the research highlighting the tendency of Fe to reduce NO [10–12]. In Daood et al. (2014, 2014), a commercial Fe-based fuel additive, for use with pulverised coal combustion, was demonstrated and discussed [13,14]. This technology was found to reduce NO emissions, reduce carbon in fly ash and increase combustion efficiency. This fuel additive technology has proven to be potentially beneficial for coal power generators and may provide the extra NO<sub>x</sub> reduction needed to comply with emission limits. However, the main constituent of the Fe-based additive, iron oxide (Fe<sub>2</sub>O<sub>3</sub>), has been reported to display SCR like properties [15]. Considering the plurality of encouraging research into the in-flame NO reduction benefits of Fe [10–14] and investigations into the effect of alternate additives on NO reduction in SNCR [16,17], it is unexpected that there is a knowledge gap regarding the potential effect of Fe on SNCR.

Previously, fuel additives for pulverised coal combustion have received a sceptical view, as seen by a 1994 European Commission

report that found many manufacturers' claims to be unjustified [18] and, later, a 2007 report by IEA Clean Coal Centre which commented on a general ineffectiveness of commercially available additives [19]. It is, therefore, categorically imperative for detailed investigation of promising additives to be undertaken to answer any outstanding questions and allow operators to benefit from technological development. Recently, there have been positive industrial trials for some new coal additives, including Pentomag 2550 I; which, when used in a coal fired boiler, was found to achieve fuel savings of 7.36% which amounted to net savings of 2038000 rupees [20].

Although fuel additives technologies have not been widely adopted, the use of process additives to boost SNCR performance has been extensively studied. This involves controlling the concentrations of reducing agents naturally found in combustion mixtures, such as hydrogen [21,22], carbon monoxide [21,23] and hydrocarbons [23,24] or introducing reagents to influence process conditions, such as hydrogen peroxide to provide a rapid source of hydroxyl radicals [25]. In general, they were found to produce desirable effects such as lowering the optimal temperature window for SNCR; however, this was accompanied by decreased maximum NO reductions, decreased selectivity and greater conversion of NO to NO<sub>2</sub>. From these studies, it is implicit that there is a desire and drive to improve SNCR performance. This drive could be legislative, environmental or economical in nature, and, as of yet, there has been little success in finding a commercially viable option. Hybrid SNCR-SCR technologies have also been demonstrated as an option to maximise NO<sub>x</sub> reduction due to SNCR, providing up to 75% reduction [26] while eliminating ammonia slip using a volumetrically smaller SCR. However, further demonstrations found issues regarding the flue gas temperature through the catalyst and arsenic poisoning of the catalyst [27].

Therefore, the aim of this study is to identify a novel hybrid of Fe-additive – SNCR to boost SNCR performance with the intention to help power generators achieve NO<sub>x</sub> legislation requirements. The objectives are: to critically assess the impact of the Fe-based additive on the use of SNCR and to evaluate the economic feasibility of such a combination. This study finds that the Fe-based additive has a positive impact on SNCR in terms of NO<sub>x</sub> reduction and reagent consumption, while also proving to be an economical option for improving SNCR performance.

## 2. Methodology

### 2.1. Pilot scale test facility

The 4 m tall pulverised fuel (PF) combustion test facility (CTF) consists of eight modular cylindrical sections with an internal diameter of 400 mm and a down-fired burner containing a fixed block swirl. The walls of the top sections behind the refractory are water-cooled to avoid temperature creep and provide stable operating conditions. The PF rig is designed up to 100 kW<sub>th</sub> input of coal ranging from 15 to 20 kg.h<sup>-1</sup> based on the calorific value of the fuel. The coal feeding arrangement contains a Rospen twin-screw feeder, with an uncertainty of ±0.5%, and a vibratory

feeding tray. The Fe-based additive is added to the coal vibratory tray through a smaller separate feeder with a single fine pitch screw. This smaller feeder can be calibrated to feed the Fe-based additive from  $0.27 \text{ kg.h}^{-1}$  to  $1 \text{ kg.h}^{-1}$ ; a 3 point calibration is done on this feeder to give repeatability confidence. The output from the vibratory tray is fed into the primary air. Due to the turbulent nature of the primary air and the length of pipe between the vibratory tray and the burner (roughly 9–10 m), it can be assumed that the additive and coal are homogeneously mixed when arriving at the burner. The majority of the combustion air is split between the primary (carrier) air and secondary air, which is supplied through a dedicated compressor and a blower fan.

The flue gas is monitored using a water-cooled probe inserted at a sample port in the eighth section located in proximity to the flue point of the CTF; this sample then passes through a series of filtration and conditioning units to remove water vapour and particulates. The sample probe is periodically purged using compressed air to remove condensed water and deposited fly ash which may block the probe or influence measurements. The concentrations of the major flue gas constituents,  $\text{NO}_x$ ,  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{O}_2$ , are measured using chemiluminescence, non-dispersive infra-red and paramagnetic based standard instruments respectively. Further details of the test facility have been discussed in Daood et al. (2014, 2014) [13,14].

The arrangement for the ammonia injection consisted of a specialized mixing skid with calibrated flowmeters for the measurement of both pure ammonia and nitrogen used as a carrier. The momentum induced by the mixed nitrogen helps induce thorough mixing of the injected ammonia into the hot gas mixture inside the furnace. The ammonia and nitrogen mixture, through a water-cooled injection probe, is introduced at the module that provides a compromise between highest possible NO reduction and lowest possible ammonia slip as discussed in Section 3.1. This arrangement benefits in the maximum reactivity of the reducing amides with the oxides of nitrogen within the optimum temperature window (850–1100 °C). The appropriate ammonia flow rate (AFR) is calculated using:

$$AFR = (NO_{initial} \times 10^{-6}) \times Q \times NSR$$

The NSR is a term used to standardise the desired  $\text{NO}_x$  reduction between different reagents, e.g. a NSR of 1 will theoretically reduce 1 mol of NO and requires 1 mol of ammonia or 0.5 mol of urea. The calculated ammonia flow rate is converted to an arbitrary flow value using the manufacturer's calibration chart.

## 2.2. Experimental method

Once the aforementioned temperature ramp from the switch to coal from propane has levelled off at  $\sim 1300$  °C, steady state is assumed to be achieved and the NO concentration in the flue gas is designated as the coal baseline level. Following the acquisition of sufficient data points, approximately 100–120 points (with one reading every ten seconds), at the coal baseline, ammonia is added at a flow rate to give a desired NSR. The NSR range under investigation is between 0 and 3. This is because during preliminary tests, it was discovered that above a NSR 3 the self-inhibition effect is observed and  $\text{NO}_x$  reduction is greatly decreased. After all the desired NSRs have been investigated, the ammonia addition ceases and there is a return to coal baseline. This confirms that no reduction in NO can be attributed to a change in initial conditions. Fe-based additive is then added and the steady state NO reduction is observed. Using the NO concentration in the flue gas for the Fe-based additive baseline as  $\text{NO}_{initial}$ , ammonia is re-introduced to the system at the same NSRs as before. Each combination of NSR and Fe-based additive concentration is observed

and recorded for approximately ten minutes. This gives a direct indication of the effect of Fe-based additive on the NO reduction by SNCR. A simplified infographic of the experimental procedure can be seen in Fig. 1.

## 2.3. Coal characterisation

The coal used to collect the data presented here is Durrans grade 240 coal, the as-received ultimate analysis and calorific value is displayed in Table 1.

## 3. Results and discussion

### 3.1. Optimisation of the SNCR: effect of the $\text{NH}_3$ injection (distance from the wall-temperature window) on the $\text{NO}_x$ reduction

A major issue concerning the implementation of SNCR regards how successfully the injected ammonia would react with the flue gas NO within the optimum temperature window. This effect has been studied by varying the dilution rate of the nitrogen, the radial injection position and the axial position for the optimum temperature window. Fig. 2 summarises the impact of the axial position with varying dilution rate of the nitrogen on the  $\text{NO}_x$  reduction and ammonia slip ( $\text{mg}/\text{Nm}^3$ ). The NO reduction rate is reduced below 1000 °C causing an increase in the ammonia slip; this could result initially in the formation of the ammonia sulphates, which usually re-condenses in the flue gas path post convective section of the boiler. Similarly, the reaction rate is slowed down above 1100 °C due to oxidation of the ammonia as evident from the near zero ammonia slip values. Usually a subtle balance must be established to gain the maximum  $\text{NO}_x$  reduction at the expense of minimum ammonia slip without compromising the overall secondary installations of the plant. This fine balance can also be greatly affected by the uniform and effective dispersion of the reducing ammonia within the flue gas path at the correct temperature window. Fig. 3 illustrates the effectiveness of the radial dispersion position of the injected ammonia towards  $\text{NO}_x$  reduction. The maximum  $\text{NO}_x$  reduction is achieved at the 150 mm radial position of the injection probe from the sidewall. The effectiveness of the homogeneous distribution of the injected ammonia has a direct impact on the reactivity rate. Nitrogen carrier flowrate of 30 L/min with injection probe at 150 mm position from the wall ensured a greater penetration depth for the reactions resulting in the highest  $\text{NO}_x$  reduction. It is evident that the overall penetration of the reducing agent, especially when injected at the right angle close to the sidewall, is less; this substantially improves at 150 mm traversed position. This could be due to the improved lateral and radial mixing of the penetrated reducing agent at that specific location.

### 3.2. Effect of Fe-based additive on SNCR

Following a simplified and prolonged procedure to that described in Section 2.2, Fig. 4 summarises the benefit of utilising the fuel enrichment process with SNCR for NSR 1.5 by presenting the NO concentration in the flue gas as the conditions in the CTF are changed, including the addition of the additive and ammonia. Fig. 4 shows that there is a clear additional benefit to the  $\text{NO}_x$  abatement potential of combining Fe-based additive with SNCR, with NO concentrations in the flue gas reducing from  $\sim 750$  ppm to  $\sim 375$  ppm. The only repeated conditions were for coal and Fe-based additive baselines. This represents the overall tolerance for the established baselines to be within 5% confidence for the CTF. The methodology adopted for this continuous data log was to highlight the varying impact of SNCR with respect to solely coal and

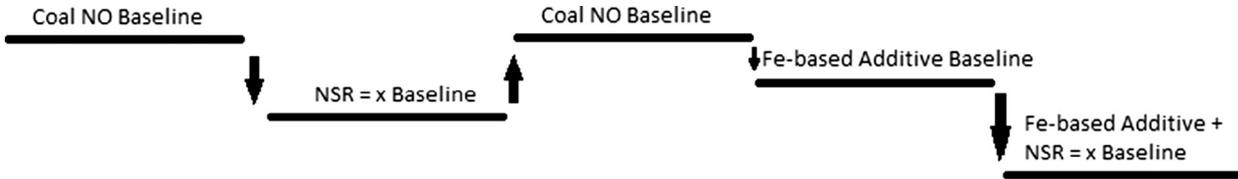


Fig. 1. Infographic of experimental procedure.

Table 1

As-received ultimate analysis of Durran's Grade 240 coal with the net fuel calorific value.

Wt%	AR
Carbon	69.2
Hydrogen	4.4
Oxygen	18.0
Nitrogen	0.8
Sulphur	0.6
Ash	3.0
Moisture	4.0
Net fuel calorific value	27.3 MJ/kg

coal with Fe-based additive. This data has been recorded for an optimum temperature window, i.e.  $1000\text{ }^{\circ}\text{C} < \text{optimum temperature window} < 1100\text{ }^{\circ}\text{C}$ , and  $\text{NSR} = 1.5$ , with  $30\text{ L/min}$  of carrier nitrogen.

Fig. 5 directly compares the NO reduction rates of SNCR with the combined SNCR-Fe-additive hybrid, including varying concentrations of the additive in the fuel, as the NSR increases. The SNCR reduction rate is with respect to the coal baseline value of NO in the flue gas and the combined reduction rates are with respect to the Fe-based additive baseline values of NO in the flue gas. Therefore, the initial NO concentration for the combination is lower and SNCR should be less effective [2].

However, Fig. 5 clearly shows greater SNCR effectiveness in the presence of Fe-based additive, indicating that the presence of the additive at the location of ammonia injection, module 5 (2.24 m axial distance from the quarl), is facilitating NO reduction due to ammonia. The low ammonia region ( $\text{NSR} < 1$ ) has a similar NO

reduction for all Fe-based additive concentrations, which is an indication that additive concentration is relatively independent to the mechanism at this stage. The reduction rates of the hybrid proceed to diverge when  $\text{NSR} > 1$ , and the concentration of additive starts to affect the effectiveness of the SNCR. The greatest reduction is observed with the greatest concentration of additive, this implies that the additive may be acting as an active site for NO reduction by ammonia. When the additive concentration is reduced, a lower reduction is observed. This could indicate that active sites on the fuel additive are becoming completely occupied and that the number of active sites limits this NO reduction mechanism; this also can lead to a negative effect on NO reduction as seen for a 1.5 NSR and 3% Fe-based additive (this is further discussed in Section 3.3 and Fig. 11). When investigating an error of two standard deviations from the mean in Fig. 5, there is obvious variation associated with the absolute NO reduction at each additive concentration; this is due to the heterogeneity of the coal's chemical composition. However, the trends associated with each condition remain confirmed on the basis of the average mean values.

Fig. 6 shows the effect of the fuel additive on ammonia utilisation efficiency of SNCR, where the ammonia utilisation efficiency is calculated using [28]:

$$\eta_{\text{NH}_3} = \frac{\text{NO}_{\text{initial}} - \text{NO}_{\text{final}}}{\text{NO}_{\text{initial}} \times \text{NSR}}$$

This property represents the proportion of reagent that is used to reduce NO, with the remaining reagent either oxidised by oxygen or lost in slip. The initial NO concentration used for the SNCR

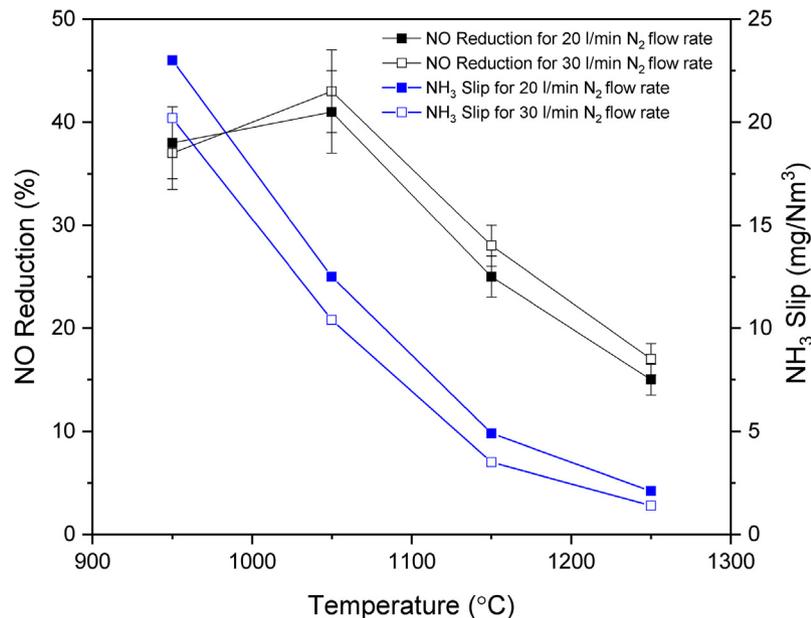


Fig. 2. NO<sub>x</sub> reduction and NH<sub>3</sub> slip as function of temperature and N<sub>2</sub> dilution rate for normalised stoichiometric ratio (NSR) 2.5.

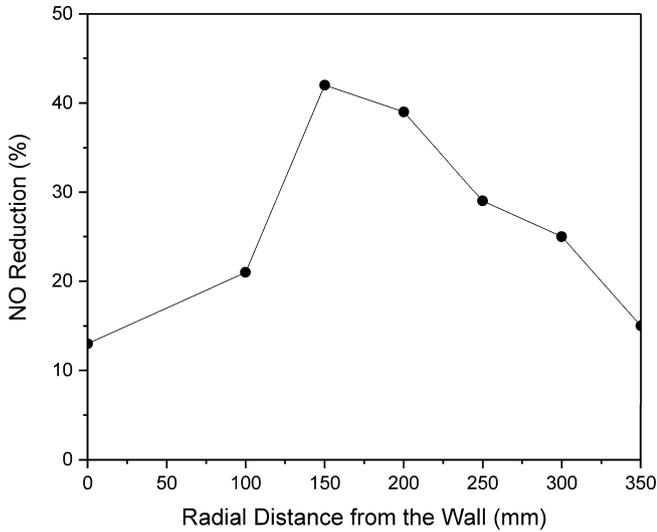


Fig. 3. NO<sub>x</sub> reduction as a function of NH<sub>3</sub> injection distance from the wall.

values is the NO in the flue gas at the coal baseline, whereas the initial NO concentration used for the hybrid is the NO in the flue gas at the Fe-based additive baseline.

Fig. 6 shows that at  $NSR \leq 1$ , the NH<sub>3</sub> utilisation efficiency is far larger for the hybrid technology; therefore, SNCR in the presence of the additive is far more effective. At  $NSR = 3$ , the efficiencies for each scenario come close to converging; this suggests that as more ammonia is introduced, the active sites become full and the SNCR NO reduction mechanism becomes the more active mechanism. This effect can be seen at lower NSRs for a lower concentration of additive, implying that there is a relationship between the two. The lack of ammonia slip is a vital parameter that also indicates a high NH<sub>3</sub> utilisation efficiency. Fig. 6 includes a representation of a two standard deviation error; this reaffirms the analysis

that there is a great increase in ammonia utilisation when the additive is present.

The reductions observed in this study may not be the highest reduction possible; this is due to two factors. One is that the residence time between ammonia injection in the CTF and flue gas may be insufficient for maximum reduction. The other is that the temperature recorded at the ammonia injection is 1100 °C ( $\pm 8$  °C); this is on the high end of the optimum temperature window for SNCR and therefore may be affected by NH oxidation system that becomes competitive with the NO reduction mechanism at  $\sim 1200$  °C.

### 3.3. Catalytic interaction between Fe-based additive and SNCR

When using Fe-based additive in conjunction with the conventional NO<sub>x</sub> abatement technique, an additional ‘bonus’ reduction was expected. This cumulative reduction was predicted to work as so: the additive would have the same effect as reported in Daood, et al. (2014, 2014) [13,14] within the quarl and the first 4 sections of the combustion test facility and then in the fifth section, the location of the ammonia injection, there would be reduction due to the selective non-catalytic properties of ammonia. However, the reduction observed did not follow the expected cumulative trend. Fig. 7 displays the observed reduction of NO concentration in the flue gas with varying degrees of additive concentration in the coal inlet compared with a number of scenarios that would have represented cumulative reduction. If a cumulative effect were taking place then the observed results would fall in line with the predicted results. Since the initial NO concentration is lower when the additive is present, due to the in-flame reduction caused by the Fe-based additive, the reduction due to SNCR will be slightly decreased [2]. Therefore, a k factor was applied to simulate that lower reduction effect; where a k factor of 0.9 indicates that the SNCR is 90% as effective compared to when the additive is not present (and the initial NO concentration is at coal baseline levels) and a k factor of 1 indicates no change in SNCR performance. The predicted results are calculated as such:

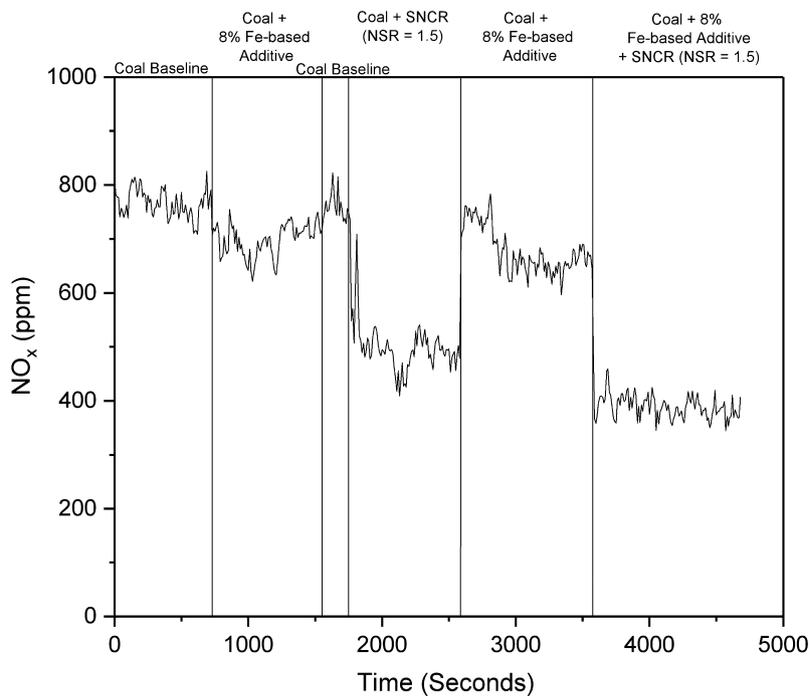


Fig. 4. Continuously logged NO emission for NSR 1.5 + 8% Fe-based fuel additive.

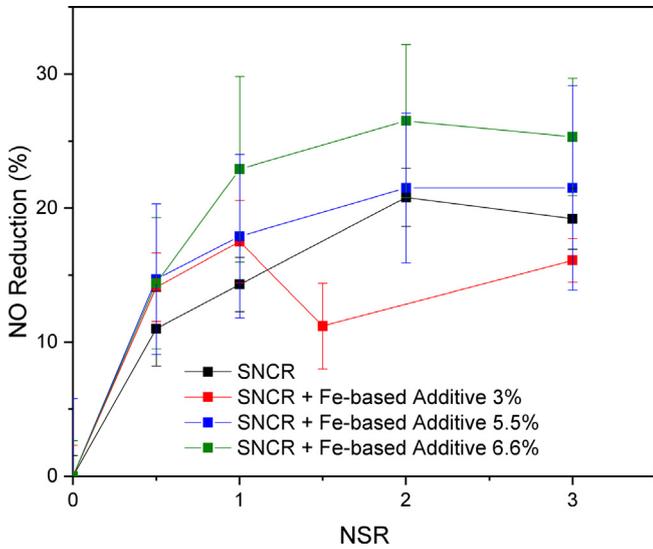


Fig. 5. NOx reductions due to SNCR in the presence of varying concentrations of Fe-based additive.

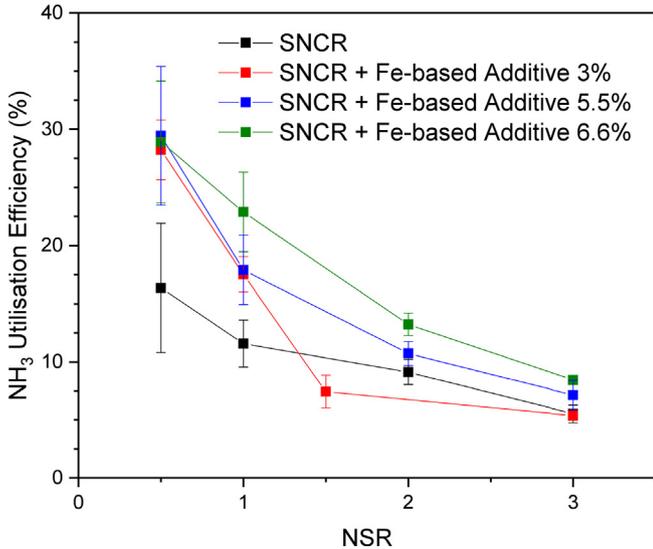


Fig. 6. Ammonia utilisation efficiency of SNCR in the presence of varying concentrations of Fe-based additive.

$$[NO]_{NSR,k} = [NO]_{additive} \times (1 - (k \times SNCR\%_{NSR}))$$

where  $SNCR\%_{NSR}$  is the NO reduction due to SNCR at a given NSR and  $[NO]_{additive}$  is the concentration of NO in the flue gas at the additive baseline.

This suggests that the cumulative reduction is not the active mechanism here. When there is assumed to be no drop in effectiveness of SNCR ( $k=1$ ), the NO reduction is not as great as observed. Under an increasing Fe-based additive concentration in the coal feed, there is a greater divergence in NO reduction between the observed results and the predicted results. The data from the trial with 3% Fe-based additive, shows that at an NSR 3, the observed NO reduction is similar to a predicted reduction with a 15% ( $k=0.85$ ) decrease in effectiveness of SNCR. However, the observed trend before this point ( $NSR \leq 1.5$ ) is vastly different from the predicted trends. This all suggests that there is an interac-

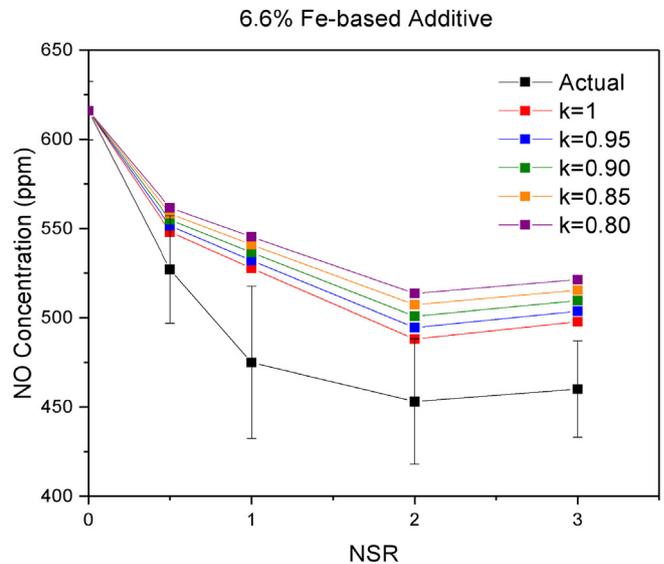
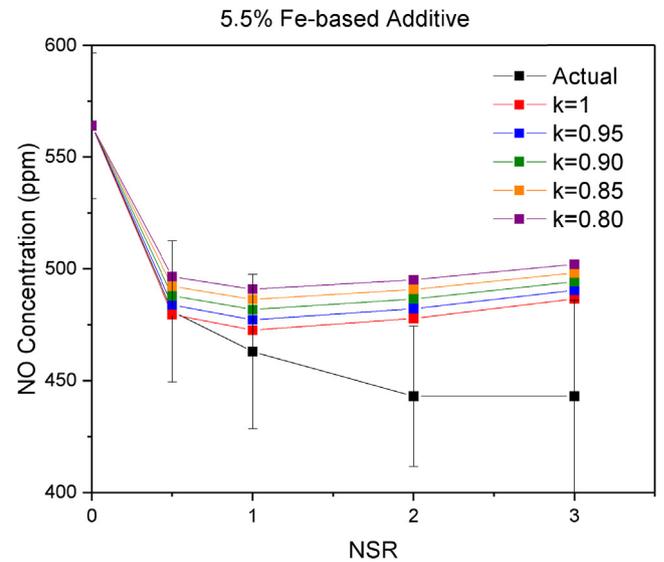
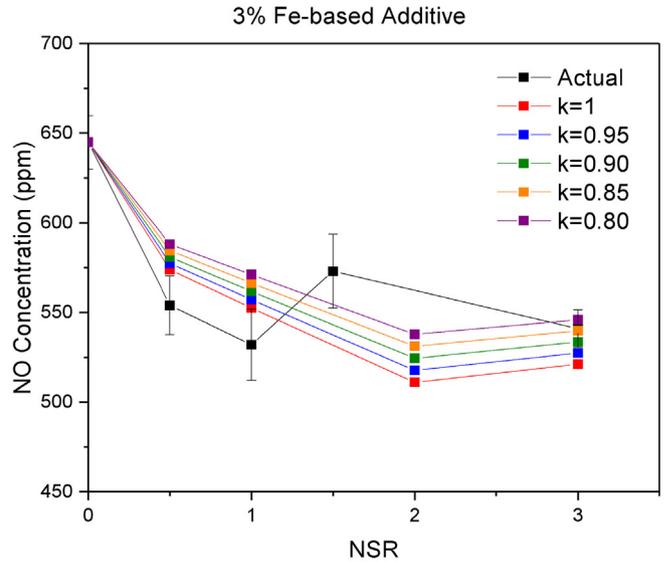


Fig. 7. Predicted additive effect compared with actual effect.

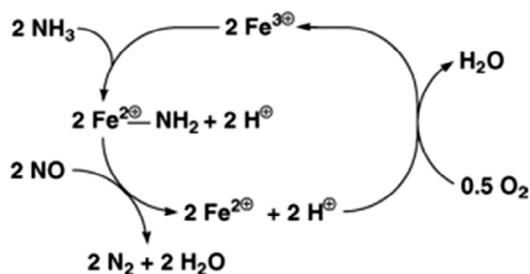


Fig. 8. Possible mechanism for ammonia-Fe interaction [13]

tion between the additive and the ammonia. When investigating the uncertainty surrounding the observed results using two standard deviations from the mean, it remains apparent that it is improbable that cumulative reduction is the active mechanism. This is summarised by the majority of the data from the k factor conditions is outside the 95% accuracy range of the observed values.

Fig. 8 shows a mechanism suggested by Apostlescu et al. (2006) [15] where iron oxide was tested as a catalyst for NO reduction by SCR. This Eley-Rideal mechanism involves an ionised iron atom acting as a binding site for the ammonia creating an amide, which in turn reduces the NO to N<sub>2</sub>, therefore facilitating the NH<sub>3</sub>/NO

reduction mechanism by removing the reliance on hydroxyl radicals to initiate the mechanism by reacting with ammonia.

Fig. 8 may, also, help explain why the fuel additive becomes detrimental for additive concentration at 3% and NSR > 1.5 (as observed in Fig. 5 and Fig. 7). As the number of active sites is exhausted, the SNCR mechanism becomes active once again and the reaction (R1) is initiated:



However, the ratio of hydroxyl radicals to ammonia molecules is very large compared to solely SNCR at the same NSR. The high hydroxyl concentration enables the reaction (R6) to compete with, and even become dominant over, reactions (R2) and (R3).



The imidogen (NH) produced from reaction (R6) is then oxidised to NO; this results in a greatly decreased NO reduction and NH<sub>3</sub> utilisation. This phenomenon is usually observed when SNCR is undertaken at a temperature far above the optimum, as the reaction rate of hydroxyl radical creation reactions are greatly increased. Returning to Fig. 5, as the NSR is increased past 1.5 the 3% additive concentration scenario shows an increase in NO reduction. The greater ammonia concentration would lead to a greater reaction rate for reaction (R1), increasing the concentration of NH<sub>2</sub> but decreasing the concentration of OH radicals. Since NH<sub>2</sub>

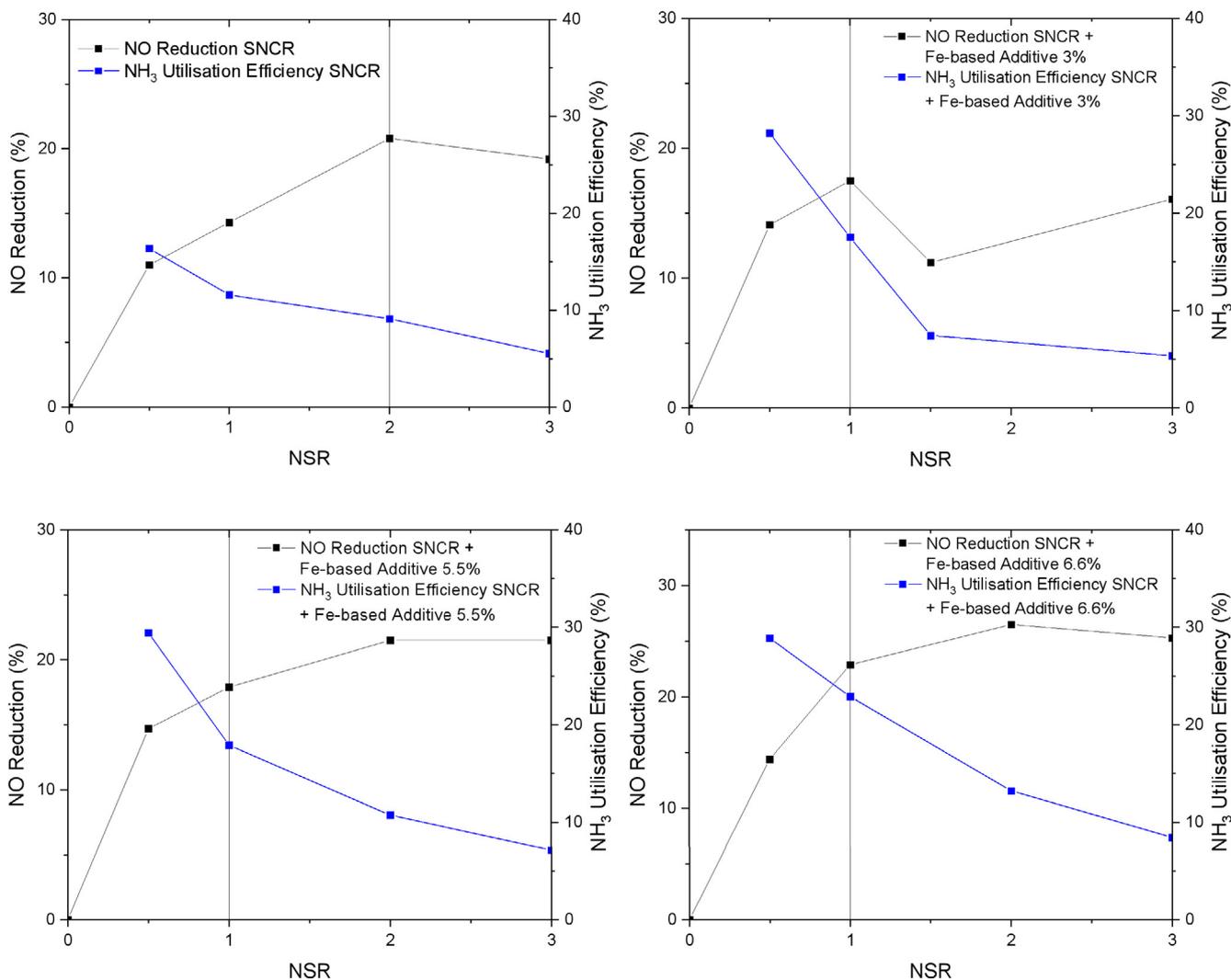


Fig. 9. Reduction in optimum NSR with the introduction of Fe-based additive.

favours reducing NO, the reaction (R6) will no longer be as competitive with the reactions (R2) and (R3), the system will stabilise and NO elimination will become greater than NO formation. A pictorial representation can be seen in Fig. 11.

Although there appears to be a catalytic type effect, this mechanism cannot be described as SCR. Within SCR systems at temperatures above  $\sim 750$  °C,  $\text{NO}_x$  reduction will rapidly decrease due to the increasing competition of ammonia combustion reactions with NO reduction reactions [29]; i.e. the system is no longer selective and will lead to low ammonia utilisation efficiency and high costs.

The Fe-based additive and SNCR hybrid technology is also far less sensitive to dust compared to conventional catalysts used in SCR applications; especially the typical catalyst poisons, which can have a substantial impact on a plant's balance sheets. The benefits of the Fe-based additive [13] have already proven to be scalable (i.e. small-scale: 100 kW<sub>th</sub> and plant-scale: 233 MW<sub>th</sub>); therefore it is also expected that the hybrid catalytic effect of the fuel additive and SNCR from the small-scale tests could be a good precursor of the full-scale demonstrations.

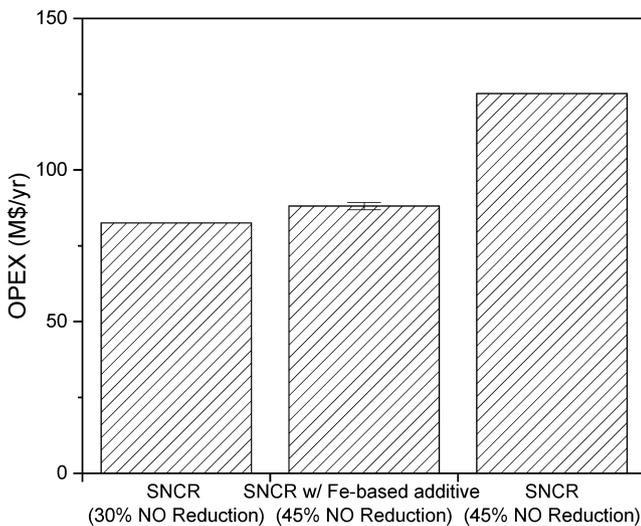


Fig. 10. Comparison of the total OPEX of different scenarios to show cost effective benefits to SNCR. Error bars represent uncertainty in Fe-based additive price.

#### 3.4. Possible economic impact of Fe-based additive

The effects on NO reduction and  $\text{NH}_3$  utilisation efficiency combine to reduce the optimum NSR for the SNCR from 2 to 1, displayed in Fig. 9. The reduction of the optimum NSR is an opportunity for pulverised coal power generators to make substantial savings on chemical costs, while continuing to meet  $\text{NO}_x$  reduction legislation. Decreasing the quantity of ammonia into the system would also have a positive effect on the potential ammonia slip; this could be key for operators that see ammonia as becoming a fully regulated pollutant.

An alternative economic benefit would be to use the additive without altering the ammonia flowrate to greatly enhance the SNCR system and achieve a greater NO reduction. This region of NO reduction would be accessible without the additive but would dramatically increase reagent costs and the likelihood of a prominent ammonia slip. Carnegie Mellon University's 'Integrated Environmental Control Model' (IECM) was used to show how effective Fe-based additive would have to be to achieve an economic benefit over increasing ammonia input. A generic 650 MW pulverised coal fired boiler was modelled with a capacity factor of 47% using a coal with an equivalent proximate make up to Durran's grade 240 coal. The  $\text{NO}_x$  emission rate was altered to 0.5202 mg/kJ to give a similar initial NO concentration to that of the flue gas during the steady state coal baseline within the CTF.

The model offers the integration of a number of environmental controls. To best simulate a conventional modern coal fired power plant, wet flue gas desulphurisation, cold side electro-static precipitators, low  $\text{NO}_x$  burners and SNCR were used. The option to include OFA was not available with SNCR. The LNBS were said to account for a 30% reduction in  $\text{NO}_x$  [1], and the SNCR was said to account for another 30% reduction [30]. The reduction capability of the SNCR was increased while observing the OPEX (operating expenditure). The NO in the flue gas followed a linear reduction while the OPEX increased dramatically and the ammonia slip increased beyond advisory levels.

Using the Fe-based additive at the baseline SNCR conditions (30%) is likely to increase the NO reduction by SNCR to  $\sim 45\%$ . The OPEX associated with using the Fe-based additive at 5.5% of the coal feed rate with SNCR operating at 30% was compared with the values of the OPEX from the IECM scenarios in which the SNCR was operating at 30% and 45% NO reduction. This comparison can

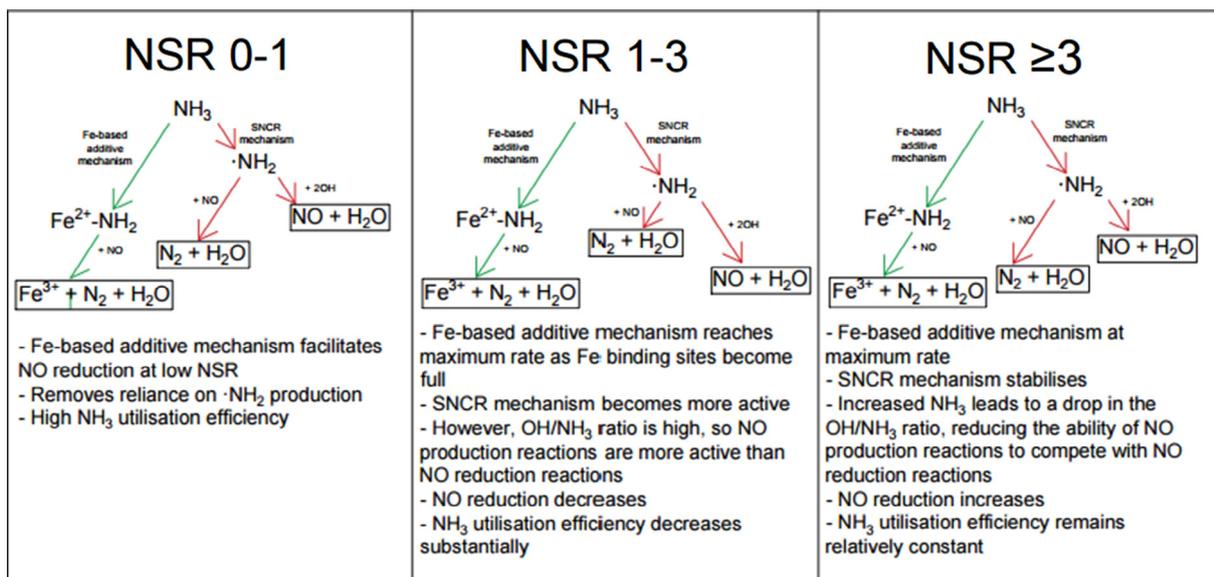


Fig. 11. Evolution of the NO related mechanisms for a Fe-based additive feed rate of 3% with increasing NSR.

be observed in Fig. 10. The OPEX for the Fe-based additive scenario was calculated by combining the estimated cost of the additive with the total OPEX of the IECM scenario in which the SNCR is running at 30%, assuming a cost of £45/ton. Fig. 10, therefore, shows that use of the Fe-based additive provides the plant operator with a unique opportunity to reduce NO<sub>x</sub> emissions while only increasing OPEX by ~\$5 M/yr compared to ~\$30 M/yr and without the worry of an unacceptable ammonia slip. The combination of the additive's in-flame NO<sub>x</sub> reduction, the NO<sub>x</sub> reduction due to LNBS and the increased effectiveness of SNCR could, cumulatively, help a plant operator to comfortably meet NO<sub>x</sub> emission limits.

This hybrid technology could even prove to be a financially viable alternative for the costly SCR system. Using the IECM, an identical plant with SCR running at 80% NO<sub>x</sub> removal and using a catalyst with a cost of \$10,000/m<sup>3</sup> [31] was simulated. This showed that although SCR would only have a slightly higher OPEX than the hybrid technology, the annualised capital cost is almost \$5million/yr greater, indicating that this is not a sustainable option for most generators. On the other hand, this figure is likely to be practically inaccurate as the model is for a new build plant. The EPA claim that retrofitting an existing boiler with SCR exhibits a higher CAPEX (capital expenditure) [32], with 30% of this increased CAPEX being attributable to demolition of structures and relocation of displaced equipment [33]. Therefore, this furthers the argument for using the fuel enrichment process in conjunction with SNCR as retrofitting is minimal and requires no down time; meaning no loss in revenue from the plant and negligible capital needed for the retrofitting process.

#### 4. Conclusions

From the data presented here, it is evident that there is an interaction between the Fe-based additive and ammonia during selective non-catalytic reduction (SNCR). A combination of these technologies can increase the NO<sub>x</sub> reduction by SNCR by >10% and provide a greater ammonia utilisation efficiency, which could decrease the chance of ammonia slip. The interaction between the technologies is theorised to be a pseudo-catalytic reaction between the ammonia and one of the major components of the fuel additive, iron oxide. The iron oxide is theorised to act as a binding site for ammonia, facilitating contact between the reagent and the NO and increasing the number of NO reduction reactions. This theory is used to explain why there is not only an increased NO reduction, but also, the greater ammonia efficiency. The possible financial benefits were analysed and a large-scale commercial furnace was simulated using the IECM to compare economic impacts. This showed that use of the Fe-additive – SNCR hybrid technology has a modest impact on the OPEX but creates a unique scenario where the NO<sub>x</sub> reduction observed would not be economically feasible when SNCR is exclusively applied. The Fe-additive – SNCR hybrid technology was also shown to be an economically viable alternative to SCR. Therefore, the hybrid is a credible alternative to hybrid SNCR/SCR and process additives for power generators wishing to improve their SNCR performance.

#### Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All the authors contributed equally.

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