



This is a repository copy of *Selective non-catalytic reduction – Fe-based additive hybrid technology*.

White Rose Research Online URL for this paper:
<http://eprints.whiterose.ac.uk/117443/>

Version: Accepted Version

Article:

Daood, S.S. orcid.org/0000-0002-4580-2504, Yelland, T. and Nimmo, W. orcid.org/0000-0001-5571-026X (2017) Selective non-catalytic reduction – Fe-based additive hybrid technology. *Fuel*, 208. pp. 353-362. ISSN 0016-2361

<https://doi.org/10.1016/j.fuel.2017.07.019>

Reuse

This article is distributed under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs (CC BY-NC-ND) licence. This licence only allows you to download this work and share it with others as long as you credit the authors, but you can't change the article in any way or use it commercially. More information and the full terms of the licence here: <https://creativecommons.org/licenses/>

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk
<https://eprints.whiterose.ac.uk/>

1 Selective non-catalytic reduction – Fe-based additive 2 hybrid technology

3 *Syed Sheraz Daood*, Thomas S. Yelland, William Nimmo*

4 Energy Engineering Group, Energy 2050, Department of Mechanical Engineering, University of
5 Sheffield, Sheffield, S10 2TN, UK.

6 HIGHLIGHTS

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

11 ABSTRACT

12 Fe-based additives can be used to improve coal combustion and reduce NO_x emissions; further to
13 this, iron oxide (Fe₂O₃) has been found to interact with ammonia. Therefore, it is critically
14 imperative to understand and assess the impact of the Fe-based additive on the use of ammonia
15 based selective non-catalytic reduction (SNCR) and to evaluate the economic feasibility of such
16 a combination for full-scale use. Experiments were performed using a 100 kWth down fired-
17 combustion test facility burning pulverised coal over three Fe-based additive concentrations,

18 while the ammonia input was varied between normalised stoichiometric ratios 0-3. This study
19 finds evidence of an interaction between the Fe-based additive and SNCR. The interaction leads
20 to greater ammonia utilisation and an increased NO_x reduction due to the SNCR of >10%. The
21 interaction is theorised to be pseudo-catalytic with the fuel additive providing an active site for
22 ammonia to reduce NO. Using Carnegie Mellon University's 'Integrated Environmental Control
23 Model' (IECM), this has been shown to create an economically viable opportunity to increase
24 SNCR effectiveness.

25 KEYWORDS

26 SNCR, NO_x , coal, additive, ammonia, Fe

27 NOMENCLATURE

28 AFR – Ammonia flow rate (ml/min)

29 η_{NH_3} – Ammonia utilisation efficiency

30 $\text{NO}_{\text{initial}}$ – The concentration of NO in the flue gas prior to ammonia injection (ppm)

31 NSR – Normalised stoichiometric ratio

32 Q – Volumetric flow rate of air (ml/min)

33

34 1. INTRODUCTION

35 The use of coal for power generation has only grown in popularity across the world in spite of
36 leading nations pledging to maximise efforts to reduce the inevitable impact of climate change,
37 in solidarity with many other future affected nations. The focus of many energy researchers is
38 therefore to create opportunities for economical clean coal technologies, particularly regarding
39 innovative SO_x and NO_x control technologies.

40 NO_x abatement technologies have been extensively reviewed [1] and are understood to be largely
41 split into two categories: combustion modification and post combustion abatement. The most
42 common combustion modification techniques include variations of low NO_x burners and over
43 fire air (OFA); these can have the unintended side-effect of reducing the combustion efficiency
44 and increasing carbon in ash [2]. Nevertheless, they are a popular choice when a European plant
45 operator is in need of economical NO_x reduction; this is due to only modest costs [2] and their
46 ability to reach the old Large Combustion Plant Directive (LCPD) (2001/20/EC) [3] emission
47 limits. Under the Industrial Emissions Directive (IED) (2010/75/EU), existing coal and biomass
48 plants over 500MW_{th} and new coal and biomass plants over 300MW_{th} in the EU are required to
49 keep their NO_x emissions below 200 mg/Nm³ [4]. In the UK, this has been a costly and laborious
50 task, and has already seen a number of coal power plants opt-out and choose to shut down [5]. In
51 China and the US, these limits are even tighter reaching 100 mg/Nm³ [6] and 117 mg/Nm³ [7]
52 respectively. These emission limits effectively require plant operators to install a post-
53 combustion abatement technology; this has forced a dilemma: accept the large financial blow but
54 secure long-term NO_x compliance with selective catalytic reduction (SCR) or install selective
55 non-catalytic reduction (SNCR) at a low cost and risk intermittent limit breaches. This is a
56 simpler choice for those running on biomass, or co-firing with biomass, as initial NO
57 concentrations tend to be far lower.

58 SCR can achieve NO_x reductions of up to 90% [2], however the catalyst that makes this possible
59 is prone to rapid fouling and the whole process is known to be very cost intensive (around
60 \$2600-7400/ton of NO reduced [8]). SNCR is seen as a less attractive prospect with a
61 substantially lower maximum removal rate (in this paper found to be ~45%); however, it is
62 relatively simple to implement [2] and far less cost intensive (around \$670-2200/ton of NO

63 reduced [8]) than SCR. SNCR is also attractive due to being unaffected by fly ash and easily
64 modified to work with other NO_x abatement technologies [9].

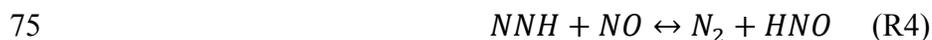
65 The technique of SNCR involves the reduction of NO by a reagent, usually ammonia or urea, at
66 a temperature window between 850 °C and 1175 °C [2]. The reagent, ammonia in this study,
67 reacts with hydroxyl radicals (OH) to form an amidogen radical (-NH₂):



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



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



76 Which leads to:



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

81 .

82 Another option would be to install SNCR while also capitalising on the research highlighting the
83 tendency of Fe to reduce NO [10] [11] [12]. In Daood, et al. (2014, 2014), a commercial Fe-
84 based fuel additive, for use with pulverised coal combustion, was demonstrated and discussed
85 [13] [14]. This technology was found to reduce NO emissions, reduce carbon in fly ash and
86 increase combustion efficiency. This fuel additive technology has proven to be potentially
87 beneficial for coal power generators and may provide the extra NO_x reduction needed to comply
88 with emission limits. However, the main constituent of the Fe-based additive, iron oxide (Fe₂O₃),
89 has been reported to display SCR like properties [15]. Considering the plurality of encouraging
90 research into the in-flame NO reduction benefits of Fe [10] [11] [12] [13] [14] and investigations
91 into the effect of alternate additives on NO reduction in SNCR [16] [17], it is unexpected that
92 there is a knowledge gap regarding the potential effect of Fe on SNCR.

93 Previously, fuel additives for pulverised coal combustion have received a sceptical view, as seen
94 by a 1994 European Commission report that found many manufacturers' claims to be unjustified
95 [18] and, later, a 2007 report by IEA Clean Coal Centre which commented on a general
96 ineffectiveness of commercially available additives [19]. It is, therefore, categorically imperative
97 for detailed investigation of promising additives to be undertaken to answer any outstanding
98 questions and allow operators to benefit from technological development. Recently, there have
99 been positive industrial trials for some new coal additives, including Pentomag 2550 I; which,
100 when used in a coal fired boiler, was found to achieve fuel savings of 7.36% which amounted to
101 net savings of 2038000 rupees [20].

102 Although fuel additives technologies have not been widely adopted, the use of process additives
103 to boost SNCR performance has been extensively studied. This involves controlling the
104 concentrations of reducing agents naturally found in combustion mixtures, such as hydrogen [21]

105 [22], carbon monoxide [21] [23] and hydrocarbons [23] [24] or introducing reagents to influence
106 process conditions, such as hydrogen peroxide to provide a rapid source of hydroxyl radicals
107 [25]. In general, they were found to produce desirable effects such as lowering the optimal
108 temperature window for SNCR; however, this was accompanied by decreased maximum NO
109 reductions, decreased selectivity and greater conversion of NO to NO₂. From these studies, it is
110 implicit that there is a desire and drive to improve SNCR performance. This drive could be
111 legislative, environmental or economical in nature, and, as of yet, there has been little success in
112 finding a commercially viable option. Hybrid SNCR-SCR technologies have also been
113 demonstrated as an option to maximise NO_x reduction due to SNCR, providing up to 75%
114 reduction [26] while eliminating ammonia slip using a volumetrically smaller SCR. However,
115 further demonstrations found issues regarding the flue gas temperature through the catalyst and
116 arsenic poisoning of the catalyst [27].

117 Therefore, the aim of this study is to identify a novel hybrid of Fe-additive - SNCR to boost
118 SNCR performance with the intention to help power generators achieve NO_x legislation
119 requirements. The objectives are: to critically assess the impact of the Fe-based additive on the
120 use of SNCR and to evaluate the economic feasibility of such a combination. This study finds
121 that the Fe-based additive has a positive impact on SNCR in terms of NO_x reduction and reagent
122 consumption, while also proving to be an economical option for improving SNCR performance.

123 **2. METHODOLOGY**

124 **2.1. Pilot Scale Test facility.**

125 The 4 m tall pulverized fuel (PF) combustion test facility (CTF) consists of eight modular
126 cylindrical sections with an internal diameter of 400 mm and a down-fired burner containing a

127 fixed block swirl. The walls of the top sections behind the refractory are water-cooled to avoid
128 temperature creep and provide stable operating conditions. The PF rig is designed up to $100 \text{ kW}_{\text{th}}$
129 input of coal ranging from $15\text{-}20 \text{ kg}\cdot\text{h}^{-1}$ based on the calorific value of the fuel. The coal feeding
130 arrangement contains a Rospen twin-screw feeder, with an uncertainty of $\pm 0.5\%$, and a vibratory
131 feeding tray. The Fe-based additive is added to the coal vibratory tray through a smaller separate
132 feeder with a single fine pitch screw. This smaller feeder can be calibrated to feed the Fe-based
133 additive from $0.27 \text{ kg}\cdot\text{h}^{-1}$ to $1 \text{ kg}\cdot\text{h}^{-1}$; a 3 point calibration is done on this feeder to give
134 repeatability confidence. The output from the vibratory tray is fed into the primary air. Due to the
135 turbulent nature of the primary air and the length of pipe between the vibratory tray and the
136 burner (roughly 9-10 m), it can be assumed that the additive and coal are homogeneously mixed
137 when arriving at the burner. The majority of the combustion air is split between the primary
138 (carrier) air and secondary air, which is supplied through a dedicated compressor and a blower
139 fan.

140 The flue gas is monitored using a water-cooled probe inserted at a sample port in the eighth
141 section located in proximity to the flue point of the CTF; this sample then passes through a series
142 of filtration and conditioning units to remove water vapour and particulates. The sample probe is
143 periodically purged using compressed air to remove condensed water and deposited fly ash
144 which may block the probe or influence measurements. The concentrations of the major flue gas
145 constituents, NO_x , CO_2 , CO and O_2 , are measured using chemiluminescence, non-dispersive
146 infra-red and paramagnetic based standard instruments respectively. Further details of the test
147 facility have been discussed in Daood et al. (2014, 2014) [13] [14].

148 The arrangement for the ammonia injection consisted of a specialized mixing skid with
149 calibrated flowmeters for the measurement of both pure ammonia and nitrogen used as a carrier.

150 The momentum induced by the mixed nitrogen helps induce thorough mixing of the injected
151 ammonia into the hot gas mixture inside the furnace. The ammonia and nitrogen mixture,
152 through a water-cooled injection probe, is introduced at the module that provides a compromise
153 between highest possible NO reduction and lowest possible ammonia slip as discussed in section
154 3.1. This arrangement benefits in the maximum reactivity of the reducing amides with the oxides
155 of nitrogen within the optimum temperature window (850 °C to 1100 °C). The appropriate
156 ammonia flow rate (*AFR*) is calculated using:

$$157 \quad AFR = (NO_{initial} \times 10^{-6}) \times Q \times NSR$$

158 The NSR is a term used to standardise the desired NO_x reduction between different reagents, e.g.
159 a NSR of 1 will theoretically reduce 1 mole of NO and requires 1 mole of ammonia or 0.5 moles
160 of urea. The calculated ammonia flow rate is converted to an arbitrary flow value using the
161 manufacturer's calibration chart.

162 2.2. Experimental method.

163 Once the aforementioned temperature ramp from the switch to coal from propane has levelled off
164 at ~1300 °C, steady state is assumed to be achieved and the NO concentration in the flue gas is
165 designated as the coal baseline level. Following the acquisition of sufficient data points,
166 approximately 100-120 points (with one reading every ten seconds), at the coal baseline,
167 ammonia is added at a flow rate to give a desired NSR. The NSR range under investigation is
168 between 0-3. This is because during preliminary tests, it was discovered that above a NSR 3 the
169 self-inhibition effect is observed and NO_x reduction is greatly decreased. After all the desired
170 NSRs have been investigated, the ammonia addition ceases and there is a return to coal baseline.
171 This confirms that no reduction in NO can be attributed to a change in initial conditions. Fe-

172 based additive is then added and the steady state NO reduction is observed. Using the NO
173 concentration in the flue gas for the Fe-based additive baseline as $\text{NO}_{\text{initial}}$, ammonia is re-
174 introduced to the system at the same NSRs as before. Each combination of NSR and Fe-based
175 additive concentration is observed and recorded for approximately ten minutes. This gives a
176 direct indication of the effect of Fe-based additive on the NO reduction by SNCR. A simplified
177 infographic of the experimental procedure can be seen in figure 1.

178 2.3. Coal characterisation.

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

181 3. RESULTS AND DISCUSSION

182 3.1. Optimisation of the SNCR: Effect of the NH_3 injection (distance from the wall- 183 temperature window) on the NO_x reduction

184 A major issue concerning the implementation of SNCR regards how successfully the injected
185 ammonia would react with the flue gas NO within the optimum temperature window. This effect
186 has been studied by varying the dilution rate of the nitrogen, the radial injection position and the
187 axial position for the optimum temperature window. Figure 2 summarises the impact of the axial
188 position with varying dilution rate of the nitrogen on the NO_x reduction and ammonia slip
189 (mg/Nm^3). The NO reduction rate is reduced below 1000 °C causing an increase in the ammonia
190 slip; this could result initially in the formation of the ammonia sulphates, which usually re-
191 condenses in the flue gas path post convective section of the boiler. Similarly, the reaction rate is
192 slowed down above 1100 °C due to oxidation of the ammonia as evident from the near zero
193 ammonia slip values. Usually a subtle balance must be established to gain the maximum NO_x

194 reduction at the expense of minimum ammonia slip without compromising the overall secondary
195 installations of the plant. This fine balance can also be greatly affected by the uniform and
196 effective dispersion of the reducing ammonia within the flue gas path at the correct temperature
197 window. Figure 3 illustrates the effectiveness of the radial dispersion position of the injected
198 ammonia towards NO_x reduction. The maximum NO_x reduction is achieved at the 150 mm radial
199 position of the injection probe from the sidewall. The effectiveness of the homogeneous
200 distribution of the injected ammonia has a direct impact on the reactivity rate. Nitrogen carrier
201 flowrate of 30 l/min with injection probe at 150 mm position from the wall ensured a greater
202 penetration depth for the reactions resulting in the highest NO_x reduction. It is evident that the
203 overall penetration of the reducing agent, especially when injected at the right angle close to the
204 sidewall, is less; this substantially improves at 150 mm traversed position. This could be due to
205 the improved lateral and radial mixing of the penetrated reducing agent at that specific location.

206 3.2. Effect of Fe-based additive on SNCR

207 Following a simplified and prolonged procedure to that described in section 2.2, figure 4
208 summarises the benefit of utilising the fuel enrichment process with SNCR for NSR 1.5 by
209 presenting the NO concentration in the flue gas as the conditions in the CTF are changed,
210 including the addition of the additive and ammonia. Figure 4 shows that there is a clear
211 additional benefit to the NO_x abatement potential of combining Fe-based additive with SNCR,
212 with NO concentrations in the flue gas reducing from ~750 ppm to ~375 ppm. The only repeated
213 conditions were for coal and Fe-based additive baselines. This represents the overall tolerance
214 for the established baselines to be within 5% confidence for the CTF. The methodology adopted
215 for this continuous data log was to highlight the varying impact of SNCR with respect to solely
216 coal and coal with Fe-based additive. This data has been recorded for an optimum temperature

217 window, i.e. $1000^{\circ}\text{C} < \text{optimum temperature window} < 1100^{\circ}\text{C}$, and $\text{NSR} = 1.5$, with 30 l/min of
218 carrier nitrogen.

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

225 However, figure 5 clearly shows greater SNCR effectiveness in the presence of Fe-based
226 additive, indicating that the presence of the additive at the location of ammonia injection, module
227 5 (2.24m axial distance from the quarl), is facilitating NO reduction due to ammonia. The low
228 ammonia region ($\text{NSR} < 1$) has a similar NO reduction for all Fe-based additive concentrations,
229 which is an indication that additive concentration is relatively independent to the mechanism at
230 this stage. The reduction rates of the hybrid proceed to diverge when $\text{NSR} > 1$, and the
231 concentration of additive starts to affect the effectiveness of the SNCR. The greatest reduction is
232 observed with the greatest concentration of additive, this implies that the additive may be acting
233 as an active site for NO reduction by ammonia. When the additive concentration is reduced, a
234 lower reduction is observed. This could indicate that active sites on the fuel additive are
235 becoming completely occupied and that the number of active sites limits this NO reduction
236 mechanism; this also can lead to a negative effect on NO reduction as seen for a 1.5 NSR and 3%
237 Fe-based additive (this is further discussed in section 3.3 and figure 11). When investigating an
238 error of two standard deviations from the mean in figure 5, there is obvious variation associated
239 with the absolute NO reduction at each additive concentration; this is due to the heterogeneity of

261 the coal's chemical composition. However, the trends associated with each condition remain
262 confirmed on the basis of the average mean values.

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

$$265 \quad \eta_{NH_3} = \frac{(NO_{initial} - NO_{final})}{(NO_{initial} \times NSR)}$$

266 This property represents the proportion of reagent that is used to reduce NO, with the remaining
267 reagent either oxidised by oxygen or lost in slip. The initial NO concentration used for the SNCR
268 values is the NO in the flue gas at the coal baseline, whereas the initial NO concentration used
269 for the hybrid is the NO in the flue gas at the Fe-based additive baseline.

270 Figure 6 shows that at $NSR \leq 1$, the NH_3 utilisation efficiency is far larger for the hybrid
271 technology; therefore, SNCR in the presence of the additive is far more effective. At $NSR = 3$,
272 the efficiencies for each scenario come close to converging; this suggests that as more ammonia
273 is introduced, the active sites become full and the SNCR NO reduction mechanism becomes the
274 more active mechanism. This effect can be seen at lower NSRs for a lower concentration of
275 additive, implying that there is a relationship between the two. The lack of ammonia slip is a
276 vital parameter that also indicates a high NH_3 utilisation efficiency. Figure 6 includes a
277 representation of a two standard deviation error; this reaffirms the analysis that there is a great
278 increase in ammonia utilisation when the additive is present.

279 The reductions observed in this study may not be the highest reduction possible; this is due to
280 two factors. One is that the residence time between ammonia injection in the CTF and flue gas
281 may be insufficient for maximum reduction. The other is that the temperature recorded at the

282 ammonia injection is 1100 °C (± 8 °C); this is on the high end of the optimum temperature
283 window for SNCR and therefore may be affected by NH oxidation system that becomes
284 competitive with the NO reduction mechanism at ~ 1200 °C.

285 3.3. Catalytic interaction between Fe-based additive and SNCR

286 When using Fe-based additive in conjunction with the conventional NO_x abatement technique,
287 an additional ‘bonus’ reduction was expected. This cumulative reduction was predicted to work
288 as so: the additive would have the same effect as reported in Daood, et al. (2014, 2014) [13] [14]
289 within the quarl and the first 4 sections of the combustion test facility and then in section 5, the
290 location of the ammonia injection, there would be reduction due to the selective non-catalytic
291 properties of ammonia. However, the reduction observed did not follow the expected cumulative
292 trend. Figure 7 displays the observed reduction of NO concentration in the flue gas with varying
293 degrees of additive concentration in the coal inlet compared with a number of scenarios that
294 would have represented cumulative reduction. If a cumulative effect were taking place then the
295 observed results would fall in line with the predicted results. Since the initial NO concentration is
296 lower when the additive is present, due to the in-flame reduction caused by the Fe-based
297 additive, the reduction due to SNCR will be slightly decreased [2]. Therefore, a k factor was
298 applied to simulate that lower reduction effect; where a k factor of 0.9 indicates that the SNCR is
299 90% as effective compared to when the additive is not present (and the initial NO concentration
300 is at coal baseline levels) and a k factor of 1 indicates no change in SNCR performance. The
301 predicted results are calculated as such:

302 $[NO]_{NSR,k} = [NO]_{additive} \times (1 - (k \times SNCR\%_{NSR}))$

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

305 This suggests that the cumulative reduction is not the active mechanism here. When there is
306 assumed to be no drop in effectiveness of SNCR ($k=1$), the NO reduction is not as great as
307 observed. Under an increasing Fe-based additive concentration in the coal feed, there is a greater
308 divergence in NO reduction between the observed results and the predicted results. The data
309 from the trial with 3% Fe-based additive, shows that at an NSR 3, the observed NO reduction is
310 similar to a predicted reduction with a 15% ($k=0.85$) decrease in effectiveness of SNCR.
311 However, the observed trend before this point ($NSR \leq 1.5$) is vastly different from the predicted
312 trends. This all suggests that there is an interaction between the additive and the ammonia. When
313 investigating the uncertainty surrounding the observed results using two standard deviations
314 from the mean, it remains apparent that it is improbable that cumulative reduction is the active
315 mechanism. This is summarised by the majority of the data from the k factor conditions is
316 outside the 95% accuracy range of the observed values.

317 Figure 8 shows a mechanism suggested by Apostlescu, et al., (2006) [15] where iron oxide was
318 tested as a catalyst for NO reduction by SCR. This Eley-Rideal mechanism involves an ionised
319 iron atom acting as a binding site for the ammonia creating an amide, which in turn reduces the
320 NO to N_2 , therefore facilitating the NH_3/NO reduction mechanism by removing the reliance on
321 hydroxyl radicals to initiate the mechanism by reacting with ammonia.

322 Figure 8 may, also, help explain why the fuel additive becomes detrimental for additive
323 concentration at 3% and $NSR > 1.5$ (as observed in figure 5 and figure 7). As the number of

324 active sites is exhausted, the SNCR mechanism becomes active once again and the reaction (R1)
325 is initiated:



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



331 The imidogen (NH) produced from reaction (R6) is then oxidised to NO; this results in a greatly
332 decreased NO reduction and NH₃ utilisation. This phenomenon is usually observed when SNCR
333 is undertaken at a temperature far above the optimum, as the reaction rate of hydroxyl radical
334 creation reactions are greatly increased. Returning to figure 5, as the NSR is increased past 1.5
335 the 3% additive concentration scenario shows an increase in NO reduction. The greater ammonia
336 concentration would lead to a greater reaction rate for reaction (R1), increasing the concentration
337 of NH₂ but decreasing the concentration of OH radicals. Since NH₂ favours reducing NO, the
338 reaction (R6) will no longer be as competitive with the reactions (R2) and (R3), the system will
339 stabilise and NO elimination will become greater than NO formation. A pictorial representation
340 can be seen in figure 11.

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

346 The Fe-based additive and SNCR hybrid technology is also far less sensitive to dust compared to
347 conventional catalysts used in SCR applications; especially the typical catalyst poisons, which
348 can have a substantial impact on a plant's balance sheets. The benefits of the Fe-based additive
349 [13] have already proven to be scalable (i.e. small-scale: 100 kW_{th} and plant-scale: 233 MW_{th});
350 therefore it is also expected that the hybrid catalytic effect of the fuel additive and SNCR from
351 the small-scale tests could be a good precursor of the full-scale demonstrations.

352 3.4. Possible economic impact of Fe-based additive

353 The effects on NO reduction and NH₃ utilisation efficiency combine to reduce the optimum NSR
354 for the SNCR from 2 to 1, displayed in figure 9. The reduction of the optimum NSR is an
355 opportunity for pulverized coal power generators to make substantial savings on chemical costs,
356 while continuing to meet NO_x reduction legislation. Decreasing the quantity of ammonia into the
357 system would also have a positive effect on the potential ammonia slip; this could be key for
358 operators that see ammonia as becoming a fully regulated pollutant.

359 An alternative economic benefit would be to use the additive without altering the ammonia
360 flowrate to greatly enhance the SNCR system and achieve a greater NO reduction. This region of
361 NO reduction would be accessible without the additive but would dramatically increase reagent
362 costs and the likelihood of a prominent ammonia slip. Carnegie Mellon University's 'Integrated
363 Environmental Control Model' (IECM) was used to show how effective Fe-based additive would
364 have to be to achieve an economic benefit over increasing ammonia input. A generic 650MW
365 pulverised coal fired boiler was modelled with a capacity factor of 47% using a coal with an
366 equivalent proximate make up to Durrans grade 240 coal. The NO_x emission rate was altered to

367 0.5202 mg/kJ to give a similar initial NO concentration to that of the flue gas during the steady
368 state coal baseline within the CTF.

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

377 Using the Fe-based additive at the baseline SNCR conditions (30%) is likely to increase the NO
378 reduction by SNCR to ~45%. The OPEX associated with using the Fe-based additive at 5.5% of
379 the coal feed rate with SNCR operating at 30% was compared with the values of the OPEX from
380 the IECM scenarios in which the SNCR was operating at 30% and 45% NO reduction. This
381 comparison can be observed in figure 10. The OPEX for the Fe-based additive scenario was
382 calculated by combining the estimated cost of the additive with the total OPEX of the IECM
383 scenario in which the SNCR is running at 30%, assuming a cost of £45/tonne. Figure 10,
384 therefore, shows that use of the Fe-based additive provides the plant operator with a unique
385 opportunity to reduce NO_x emissions while only increasing OPEX by ~\$5M/yr compared to
386 ~\$30M/yr and without the worry of an unacceptable ammonia slip. The combination of the
387 additive's in-flame NO_x reduction, the NO_x reduction due to LNBS and the increased
388 effectiveness of SNCR could, cumulatively, help a plant operator to comfortably meet NO_x
389 emission limits.

390 This hybrid technology could even prove to be a financially viable alternative for the costly SCR
391 system. Using the IECM, an identical plant with SCR running at 80% NO_x removal and using a
392 catalyst with a cost of \$10,000/m³ [31] was simulated. This showed that although SCR would
393 only have a slightly higher OPEX than the hybrid technology, the annualised capital cost is
394 almost \$5million/yr greater, indicating that this is not a sustainable option for most generators.
395 On the other hand, this figure is likely to be practically inaccurate as the model is for a new build
396 plant. The EPA claim that retrofitting an existing boiler with SCR exhibits a higher CAPEX
397 (capital expenditure) [32], with 30% of this increased CAPEX being attributable to demolition of
398 structures and relocation of displaced equipment [33]. Therefore, this furthers the argument for
399 using the fuel enrichment process in conjunction with SNCR as retrofitting is minimal and
400 requires no down time; meaning no loss in revenue from the plant and negligible capital needed
401 for the retrofitting process.

402 4. CONCLUSIONS

403 From the data presented here, it is evident that there is an interaction between the Fe-based
404 additive and ammonia during selective non-catalytic reduction (SNCR). A combination of these
405 technologies can increase the NO_x reduction by SNCR by >10% and provide a greater ammonia
406 utilisation efficiency, which could decrease the chance of ammonia slip. The interaction between
407 the technologies is theorised to be a pseudo-catalytic reaction between the ammonia and one of
408 the major components of the fuel additive, iron oxide. The iron oxide is theorised to act as a
409 binding site for ammonia, facilitating contact between the reagent and the NO and increasing the
410 number of NO reduction reactions. This theory is used to explain why there is not only an
411 increased NO reduction, but also, the greater ammonia efficiency. The possible financial benefits
412 were analysed and a large-scale commercial furnace was simulated using the IECM to compare

413 economic impacts. This showed that use of the Fe-additive - SNCR hybrid technology has a
414 modest impact on the OPEX but creates a unique scenario where the NO_x reduction observed
415 would not be economically feasible when SNCR is exclusively applied. The Fe-additive - SNCR
416 hybrid technology was also shown to be an economically viable alternative to SCR. Therefore,
417 the hybrid is a credible alternative to hybrid SNCR/SCR and process additives for power
418 generators wishing to improve their SNCR performance.

419 AUTHOR INFORMATION

420 **Corresponding Author**

421 * Dr. Syed Sheraz Daood, Level 1, Arts Tower, Energy Engineering Group, Energy 2050,
422 Department of Mechanical Engineering, University of Sheffield, Sheffield, S10 2TN, UK.

423 Email: s.daood@sheffield.ac.uk; speme@hotmail.co.uk

424 **Author Contributions**

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

427

428

429 **Acknowledgement**

430 The authors are grateful to International Innovative Technologies UK Ltd (Unit 5 Queens Court,
431 Third Avenue, Team Valley Trading Estate, Gateshead, NE11 0BU) for providing access to the
432 test facility and Fe-based additive for this research.

433 REFERENCES

- 434 [1] Skalska K, Miller JS, Ledakowicz S. Trends in NO_x abatement: A review. Science of the
435 Total Environment, 2010; 408: 3976-89.
- 436 [2] Javed MT, Irfan N, Gibbs BM. Control of combustion-generated nitrogen oxides by selective
437 non-catalytic reduction. Journal of Environmental Management, 2007; 83: 251-89.
- 438 [3] European Union. Large Combustion Plants Directive, 2001/20/EC, Brussels, Belgium.
- 439 [4] European Union. Industrial Emissions Directive, 2010/75/EU, Brussels, Belgium.
- 440 [5] DECC. Running hours during winter 2013/14 for plants opted-out of the Large Combustion
441 Plant Directive (LCPD),
442 https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/357531/LCPD.pdf
443 ; 2014 [accessed 26.03.17].
- 444 [6] IEA Clean Coal Centre. Emissions standards: China, [http://www.iea-](http://www.iea-coal.org.uk/documents/82539/9516/China)
445 [coal.org.uk/documents/82539/9516/China](http://www.iea-coal.org.uk/documents/82539/9516/China); 2015 [accessed 22.05.17].
- 446 [7] IEA Clean Coal Centre. Emissions standards: USA, [http://www.iea-](http://www.iea-coal.org.uk/documents/82575/9515/United%20States%20of%20America)
447 [coal.org.uk/documents/82575/9515/United%20States%20of%20America](http://www.iea-coal.org.uk/documents/82575/9515/United%20States%20of%20America); 2015 [accessed
448 22.05.17].
- 449 [8] Neuffer B. NO_x Controls for Existing Utility Boilers,
450 <https://www.epa.gov/sites/production/files/2015-07/documents/nescam2.pdf>; 2015 [accessed
451 26.03.17].
- 452 [9] Hampartsoumian E, Folayan OO, Nimmo W, Gibbs BM. Optimisation of NO_x reduction in
453 advanced coal reburning systems and the effect of coal type. Fuel, 2003; 82: 373-84.

454 [10] Lissianski VV, Maly PM, Zamansky VM, Gardner WC. Utilization of Iron Additives for
455 Advanced Control of NO_x Emissions from Stationary Combustion Sources. Industrial and
456 Engineering Chemistry Research, 2001; 40: 3287-93.

457 [11] Fennell PS and Hayhurst AN. The kinetics of the reduction of NO to N₂ by reaction with
458 particles of Fe. Proceedings of the Combustion Institute, 2002; 2179-2185.

459 [12] Lasek JA. Investigations of the reduction of NO to N₂ by reaction with Fe under fuel-rich
460 and oxidative atmosphere. Heat Mass Transfer, 2014; 50: 933-43.

461 [13] Daood SS, Ord G, Wilkinson T, Nimmo W. Fuel additive technology – NO_x reduction,
462 combustion efficiency and fly ash improvement for coal fired power stations. Fuel, 2014; 134:
463 293-306.

464 [14] Daood SS, Ord G, Wilkinson T, Nimmo, W. Investigation of the Influence of Metallic Fuel
465 Improvers on Coal Combustion/Pyrolysis. Energy & Fuels, 2014; 28: 1515-23.

466 [15] Apostolescu N, Geiger B, Hizbullah K, Jan MT, Kureti S, Reichert D, et al. Selective
467 catalytic reduction of nitrogen oxides by ammonia on iron oxide catalysts. Applied Catalysis B:
468 Environmental, 2006; 62: 104-114.

469 [16] Li T, Zhuo Y, Chen C, Xu X. Effect of CaO on NH₃+ NO + O₂ reaction system in the
470 absence and presence of high concentration CO₂. Asia-Pacific Journal of Chemical Engineering,
471 2010; 5: 287-293.

472 [18] Hao J, Yu W, Lu P, Zhang Y, Zhu Y. The effects of Na/K additives and flyash on NO
473 reduction in a SNCR process. Chemosphere, 2015; 122: 213-218.

474 [18] European Commission. The Role of Fuel Additives to Control Environmental Emissions
475 and Ash Fouling, [https://bookshop.europa.eu/en/the-role-of-fuel-additives-to-control-](https://bookshop.europa.eu/en/the-role-of-fuel-additives-to-control-environmental-emissions-and-ash-fouling-pbCDNA14893/)
476 [environmental-emissions-and-ash-fouling-pbCDNA14893/](https://bookshop.europa.eu/en/the-role-of-fuel-additives-to-control-environmental-emissions-and-ash-fouling-pbCDNA14893/); 1994 [accessed 26.03.17].

477 [19] IEA Clean Coal Centre. Significant achievements of European Coal and Steel Community
478 R&D programmes in the development of clean coal power generation technology,
479 <http://www.iea-coal.org.uk/documents/81741/6388/Clean-coal-technology-R,D&D;> 2007
480 [accessed 26.03.17].

481 [20] TELLABS Chemicals Private Limited. Tellabs Trial Report for PENTOMAG 2550 I - Coal
482 Additive, https://www.pentol.net/sites/default/files/pentomag2550-trial_naachiar-india.pdf; 2013
483 [accessed 26.03.17]

484 [21] Javed MT, Nimmo W, Gibbs BM. Experimental and modeling study of the effect of CO and
485 H₂ on the urea DeNO_x process in a 150 kW laboratory reactor. *Chemosphere*, 2008; 70: 1059-
486 67.

487 [22] Lyon RK and Hardy JE. Discovery and Development of the Thermal DeNO_x Process.
488 *Industrial & Engineering Chemistry Fundamentals*, 1988; 25: 19-24.

489 [23] Bae SW, Roh SA, Kim SD. NO removal by reducing agents and additives in the selective
490 non-catalytic reduction (SNCR) process. *Chemosphere*, 2006; 65: 170-5.

491 [24] Wenli D, Dam-Johansen K, Østergaard K. Widening the temperature range of the thermal
492 DeNO_x process, an experimental investigation. 23rd Symposium (International) on Combustion,
493 The Combustion Institute, Pittsburgh, 1990; 297–303.

494 [25] Azuhata S, Akimoto H, Hishinuma Y. Effect of H₂O₂ on homogenous gas phase NO
495 reduction reaction with NH₃. *AIChE Journal*, 1982; 28: 7-11.

496 [26] Urbas J and Boyle JM. Design, Optimization and Economic Analysis of SNCR/SCR Hybrid
497 on a Utility Boiler in the Ozone Transport Region. 1998 American/Japanese Flame Research
498 Committees International Symposium, 1998.

499 [27] Urbas, J.B. Hybrid selective non-catalytic reduction (SNCR)/selective catalytic (SCR)
500 demonstration for the removal of NO_x from boiler flue gases.
501 [http://citeseerx.ist.psu.edu/viewdoc/download;jsessionid=1F7EF09CE1134A492C78949FD262C](http://citeseerx.ist.psu.edu/viewdoc/download;jsessionid=1F7EF09CE1134A492C78949FD262C667?doi=10.1.1.172.3627&rep=rep1&type=pdf)
502 [667?doi=10.1.1.172.3627&rep=rep1&type=pdf](http://citeseerx.ist.psu.edu/viewdoc/download;jsessionid=1F7EF09CE1134A492C78949FD262C667?doi=10.1.1.172.3627&rep=rep1&type=pdf); 1999 [accessed 26.03.17].

503 [28] Daood SS, Javed MT, Gibbs BM, Nimmo W. NO_x control in coal combustion by
504 combining biomass co-firing, oxygen enrichment and SNCR. *Fuel*, 2013;105: 283-92.

505 [29] Horvath IT. *Encyclopedia of Catalysis: Volume 5*. Hoboken, New Jersey: John Wiley &
506 Sons Inc.; 2003.

507 [30] Gomez-Garcia MA, Pitchon V, Kiennemann A. Pollution by nitrogen oxides: an approach
508 to NO_x abatement by using sorbing catalytic materials. *Environment International*, 2005; 31:
509 445-67.

510 [31] EPA. EPA-CICA Fact Sheet: SCR. <https://www3.epa.gov/ttnecat1/dir1/fscr.pdf>; 2003
511 [accessed 26.03.17].

512 [32] EPA. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards.
513 EPA Air Pollution Control Cost Manual Section 4 Chapter 2.
514 https://www3.epa.gov/ttnecat1/dir1/c_allchs.pdf; 2000 [accessed 26.03.17].

515 [33] Cochran JR, Gregory MG, Rummenhohl V. The Effect of Various Parameters on SCR
516 System Cost. Presented at Power-Gen '93, the Fourth International Power Generation Exhibition
517 & Conference, ASME, Dallas, Texas, November 1993



Figure 1 - Infographic of Experimental Procedure

Table 1 - As-received ultimate analysis of Durrans 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

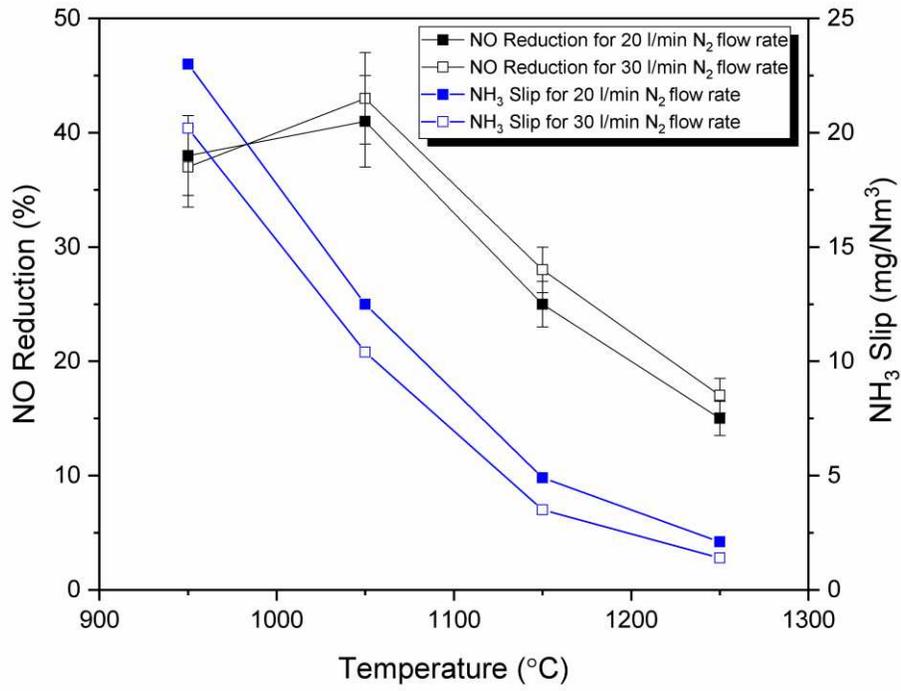


Figure 2 - NO_x reduction and NH₃ slip as function of temperature and N₂ dilution rate for normalised stoichiometric ratio (NSR)

2.5

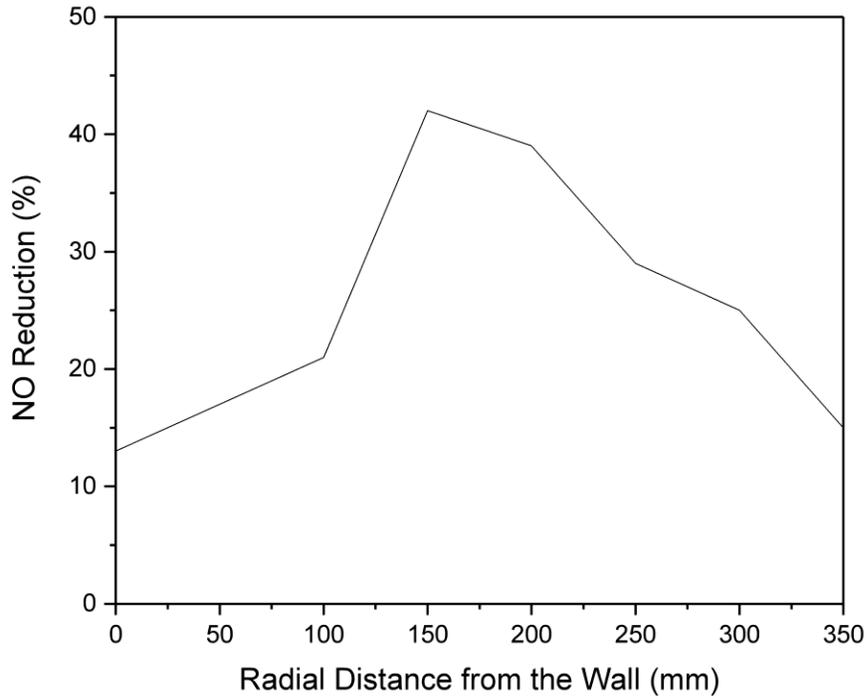


Figure 3 - NO_x reduction as a function of NH₃ injection distance from the wall

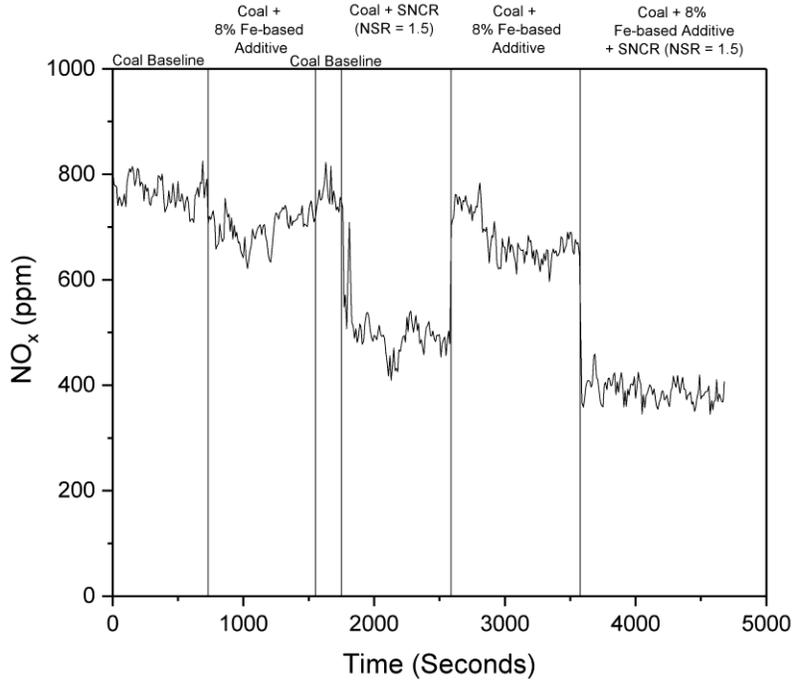


Figure 4 - Continuously logged NO emission for NSR 1.5 + 8% Fe-based fuel additive

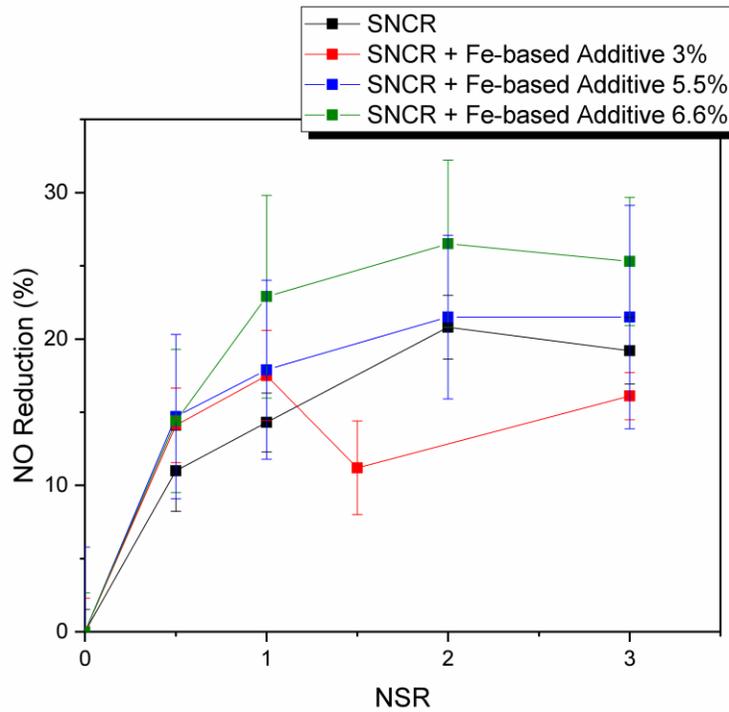


Figure 5 – NOx reductions due to SNCR in the presence of varying concentrations of Fe-based additive

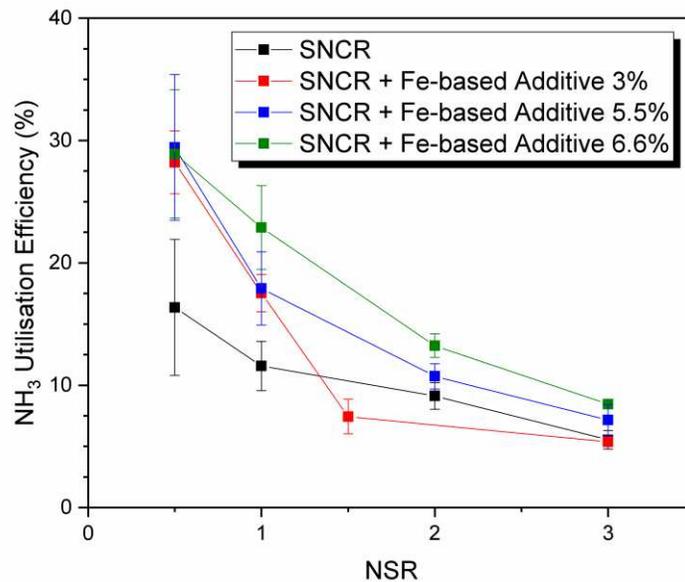


Figure 6 – Ammonia utilisation efficiency of SNCR in the presence of varying concentrations of Fe-based additive

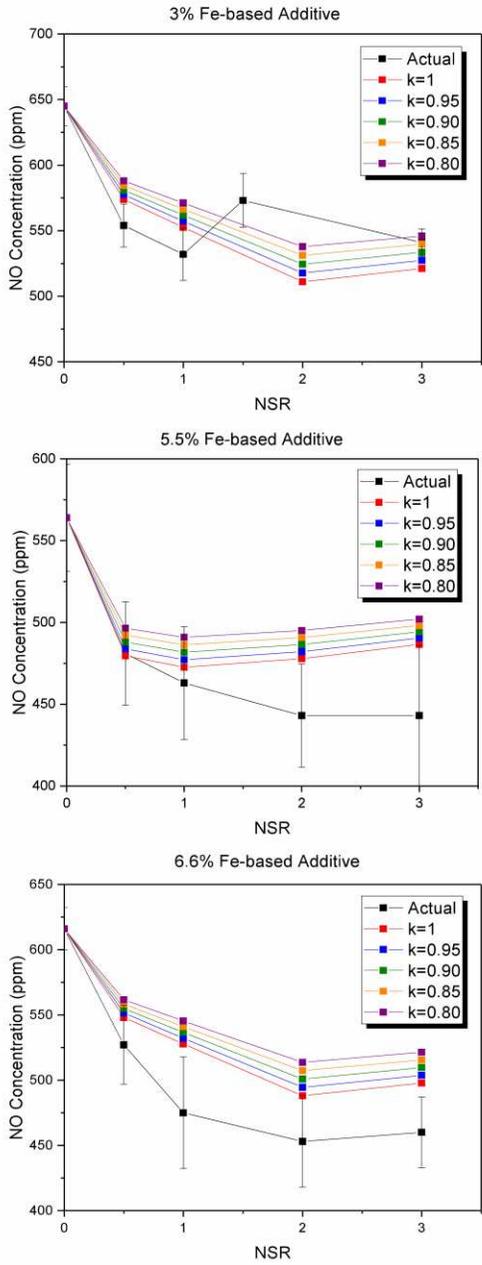


Figure 7 - Predicted Additive Effect Compared with Actual Effect

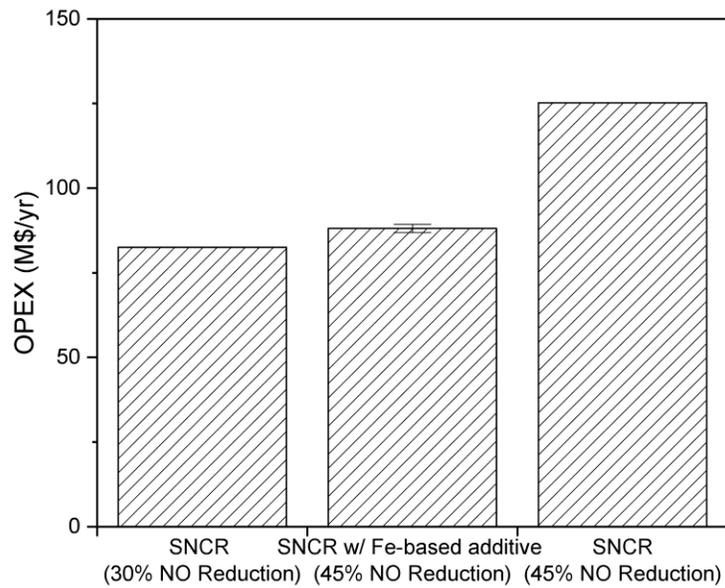


Figure 10 – Comparison of the total OPEX of different scenarios to show cost effective benefits to SNCR. Error bars represent uncertainty in Fe-based additive price.

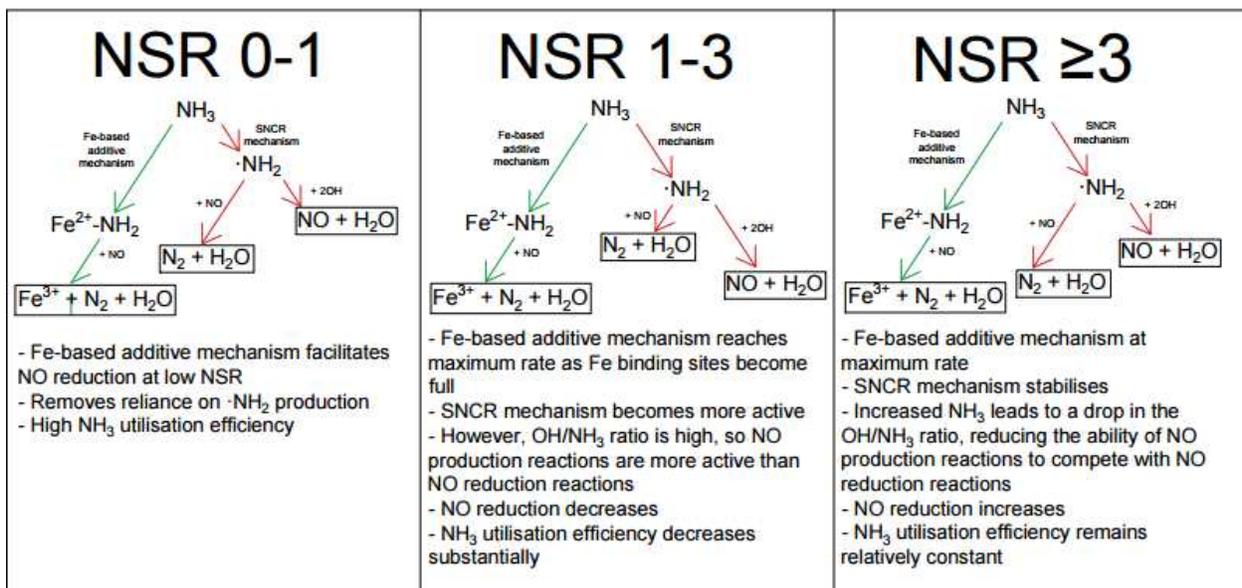


Figure 11 – Evolution of the NO related mechanisms for a Fe-based additive feed rate of 3% with increasing NSR