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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_x emissions; further to this, iron oxide (Fe_2O_3) 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_x 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.

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_x and NO_x control technologies.

NO_x 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_x 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_x 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 $500MW_{th}$ and new coal and biomass plants over 300MWth in the EU are required to keep their NO_x emissions below 200 mg/Nm^3 [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^3 [6] and 117 mg/Nm^3 [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_x 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
ηNH_3	ammonia utilisation efficiency	Q	volumetric flow rate of air (ml/min)
$NO_{initial}$	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_x 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_x 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 ($-NH_2$):

$$NH_3 + OH \leftrightarrow NH_2 + H_2O \tag{R1}$$

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

$$NH_2 + NO \leftrightarrow N_2 + H_2O \tag{R2}$$

$$NH_2 + NO \leftrightarrow NNH + OH \tag{R3}$$

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:

$$NNH + NO \leftrightarrow N_2 + HNO \tag{R4}$$

Which leads to:

$$HNO + M \leftrightarrow H + NO + M \tag{R5}$$

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_x reduction needed to comply with emission limits. However, the main constituent of the Fe-based additive, iron oxide (Fe_2O_3), 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_2. 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_x 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_x 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_x 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_{th} input of coal ranging from 15 to 20 $kg.h^{-1}$ 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