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**Article:**

Daood, S.S., Ord, G., Wilkinson, T. et al. (1 more author) (2014) Fuel additive technology - NO<sub>x</sub> reduction, combustion efficiency and fly ash improvement for coal fired power stations. *Fuel*, 134. 293 - 306. ISSN 0016-2361

<https://doi.org/10.1016/j.fuel.2014.04.032>

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1 Fuel Additive Technology - NOx Reduction, combustion efficiency and fly ash  
2 improvement for coal fired power stations

3  
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10  
11 **Abstract**

12 Fuel additive technology is based on the use of a solid, fuel additive (iron, aluminium, calcium and silicon  
13 based oxides), to reduce NOx emission, improve the quality of fly ash and result in 1-3% coal savings for  
14 pulverised coal combustion. The findings in this study have been mainly based on extensive  
15 experimentation on 100kWth down fired-combustion test facility (CTF) and partially on a 260tons/hr  
16 steam commercial producing water tube pf boiler. International Innovative Technologies (IIT) developed  
17 this additive based technology for the combined effect of reducing NOx from the combustion of  
18 hydrocarbon fuels (mainly coal) and more specifically to improve the combustion process of fossil fuels  
19 resulting in an ash by product with improved loss on ignition and lower carbon content. The improvement  
20 in the combustion thermal efficiency of the commercial 260tons/hr steam producing boiler has been  
21 calculated as per the direct calculation method of EN BS12952-15:2003 standard.  
22  
23

24 Keywords: Fuel, additive, NOx, fly ash, combustion efficiency, coal, boiler, BS EN12952-15 (2003).

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26  
27

28 **1. Introduction**

29 The consumption of coal is increasing continuously on a global scale and is likely to  
30 increase in forthcoming years due to its cheaper pricing compared with other conventional fuels  
31 and further economic expansion in developing countries. However, the environmental  
32 regulations and legislation has enforced a rise in carbon floor pricing and heavy penalties  
33 towards breaching caps on emissions. In USA, the environmental protection agency has

34 proposed to implement 1,100 pounds (499 kgs) of cap on CO<sub>2</sub> emissions generated for every  
35 MWh of electricity produced from June 1, 2014 [1]. Similarly clean air interstate rule (CAIR)  
36 has a total of 1,882,226 tons (170756 tonne) of NO<sub>x</sub> allowance, which is annually reconciled to  
37 check and ensure that NO<sub>x</sub> emissions reduction is strictly monitored and consequently controlled  
38 [2]. Amongst EU states, businesses are penalised if they do not have enough allowances for each  
39 calendar year to cover emissions; e.g. for 2013, penalty charges were € 100 per tonne of CO<sub>2</sub> (or  
40 the equivalent amount of N<sub>2</sub>O) [3]. It is also noteworthy that the fly ash handling and disposal  
41 costs are increasing due to the higher carbon content carrying fly ash. It is of particular interest in  
42 finding systems to reduce or minimize the emissions, improve thermal efficiency, and utilise  
43 efficiently the fly ash product through catalysts or additives. The fuel improver is capable of  
44 reducing emissions, increasing thermal efficiency and produce low carbon fly ash to be used in  
45 cement industry. The technology is already patented and findings have been endorsed in UK  
46 Patent GB 2462978 and pending UK patent application No 1308472.8.

47 Hence it is of pivotal importance to the power plants in particular to operate and have  
48 enough allowances to cover emissions specially CO<sub>2</sub> and NO<sub>x</sub>. Similarly, excessive carbon  
49 remaining in the fly ash affects the optimum density and moisture content for filling application  
50 in the building industry along with less protection against freeze thaw conditions. Fly ash can be  
51 used as a replacement for a proportion of Portland cement content of concrete mixture resulting  
52 in indirect savings in CO<sub>2</sub> emissions since cement industry produces approximately one tonne of  
53 CO<sub>2</sub>/ ton of Portland cement.

54 During recent years influences of different additives/catalysts on combustion behaviour  
55 have been investigated [4-8]. The iron-based catalyst improved pyrolysis yield and char  
56 oxidation rates at high temperatures even at high heating rates [4]. In another study when Fe<sup>+3</sup>

57 ions were added to the demineralised coal samples via precipitation method, N<sub>2</sub> formation from  
58 char-N increased by two folds [5]. Similarly cluster of iron oxides are known to reduce NO to  
59 form N<sub>2</sub> [6]. Iron based fuel improvers because of relatively better heat transfer properties could  
60 also enhance thermal cracking of heavier hydrocarbon supported by increase in hydrocarbon  
61 intensities and Volatile-N [7]. At high temperature and water concentration, reactivity of Fe<sub>2</sub>O<sub>3</sub>  
62 during reburning is increased due to oxidative ability and HCN oxidation to CO and N<sub>2</sub>,  
63 respectively [8].

64 The proof of the concept to utilise IIT's fuel additive that has already been tested on  
65 smaller - bench scale reactor and has progressed through pilot scale and to commercial 260  
66 ton/hr. The results of the pilot and full scale tests are presented here.

## 67 **2. Experimental test facilities and methods**

68 The pilot scale combustion test facility (CTF) comprises of a down-fired pulverised coal  
69 furnace. The furnace has eight modular sections with each having an internal diameter of 400mm  
70 (Figure 1a). The overall furnace is 4 meter in height. The input feed rate of an approximately 10-  
71 11.65 kg/hr of coal (depending upon types of coal) result in a net thermal input of about 75-85  
72 kW to the CTF. The coal was fed in the CTF through Rospen's loss in weight feeder (Figure  
73 1b), whereas fuel additive was blended in the vibratory tray with help of smaller vibratory feeder  
74 (Figure 1c). The down-fired quartz section of the burner expands from 66mm throat to 475mm  
75 diameter. Initially the CTF is warmed up with propane until temperature around the burner is  
76 1000°C for transitioning fuel from propane to coal. The coal firing continues until temperature  
77 reaches steady state. To minimise temperature creep in the system the top sections are water-  
78 jacketed and insulated.. The major flue gas species (CO<sub>2</sub>, O<sub>2</sub>, NO<sub>x</sub>, and CO) are measured at the  
79 outlet of furnace through water cooled stainless steel probe to the gas sampling system. The

80 continuous emission measurements of O<sub>2</sub>, CO<sub>2</sub>, CO, and NO (NO<sub>x</sub>) and temperatures throughout  
81 the furnace are logged to spread sheet during each test period. The fuel additive was fed with  
82 different types of coal to the furnace in mass fractions from 1.3% to 13%. A dedicated cyclone  
83 separator collects the fly ash from flue gas path. The analysis on emissions was only performed  
84 on steady state and collected coal fly ash samples were analysed as per ASTM D7348-08 for loss  
85 on ignition (LOI).

86 The commercial trials have been performed on a natural circulation, front wall fired  
87 boiler with maximum continuous rating steam flow generation of about 280 tons/hr when firing  
88 coal. There are twelve burners set in 3 landings of 4 burners each. Each landing of the boiler (4  
89 burners) is connected with vertical ball mill. Two forced draft (FD) fans supply the primary and  
90 secondary air for the boiler whereas two induced draft (ID) fans draw the exhaust gases through  
91 the air heater and an electrostatic precipitator before discharging the gases to the stack. The  
92 overall process flow diagram of the boiler is shown in Figure 2. The direct method was adopted  
93 to calculate the boiler efficiency due to the relative size of the boiler and highest accuracy in  
94 measurements. It is worth mentioning that this commercial boiler does not have steam re-heaters,  
95 steam air heater, flue gas recirculation or circulating pump arrangements.

96 The following were the calculations utilized for the purpose of determining the Thermal  
97 efficiency of the boiler (BS EN 12952-15:2003).

98

$$99 \quad \eta (N)B = \frac{Q_N}{Q_{(N)Ztot}}$$

$$Q_N = m_{ST}(h_{ST} - h_{FW}) + m_{SS}(h_{FW} - h_{SS})$$

$$100 \quad Q_{(N)Ztot} = m_F H_{(N)tot} + Q_{(N)Z}$$

101 Where

$$Q_{(N)Z} = P_M + P$$

$$H_{(N)tot} = (H_{(N)} + C_F(t_F - t_r)) / (1 - l_u) + \mu_{AS}h_{(N)AS} + \mu_A C_{pA}(t_A - t_r)$$

$$l_u = \frac{\gamma_{Ash}(1-v)}{1-\gamma_{Ash}-\gamma_{H2O}} \left[ \frac{u_{SL}}{1-u_{SL}} \eta_{SL} + \frac{u_{FA}}{1-u_{FA}} \eta_{FA} \right] \text{ (Based on estimated ash collection efficiency)}$$

The above  $Q_{(N)Ztot}$  equation gets simplified into the following equation 1; when running on coal;

$$Q_{(N) Ztot} = m_F \left[ (H_{(N)} + C_F(t_F - t_r)) / \left[ 1 - \frac{\gamma_{Ash}(1-v)}{1-\gamma_{Ash}-\gamma_{H2O}} \left( \frac{u_{SL}}{1-u_{SL}} \eta_{SL} + \frac{u_{FA}}{1-u_{FA}} \eta_{FA} \right) \right] + \mu_A C_{pA}(t_A - t_r) \right] + P_M + P$$

..... (1)

The measurements associated with stack emissions, coal flow, primary and secondary air flows, boiler and spray feed water flow rates, main steam flow and associated temperature and pressure were recorded during the trials. The recorded data under steady state was analysed using the following statistical techniques. Statistical average was applied on the data in order to acquire the steady state levels. The statistical analysis of the data included the standard deviation and the average. The standard deviation gave an indication of how widely values are dispersed from the average value (mean). It explains how much variation or dispersion from the average mean.

**2.1. Material**

Additive is mainly a mixture of iron, aluminium, calcium and silicon oxides. It is low cost synthetic mineral with a strongly bonded matrix structure of different elements. Two of the types of additives can be produced; a: Air Cooled Additive, b: Water Cooled Additive. The XRF/XRD composition of the both these types are tabled below (Table 1).

Table 2 shows the particle size distribution of both types of Additive milled in IIT M600 patent mills (GB 2451299, GB 2460505, and GB 2471934). It is recommended to have the processed Additive milled at 90th percentile equal or less than 32 μm [d (0.9) ≤ 32], this would

121 benefit in minimum impact towards rate of abrasion in normally basalt lined Pf lines. It has been  
122 suggested in literature [9-10] that generally the erosive wear increases with the cube of particle  
123 size, hence by keeping the milled particle size distribution less than 25 microns the rate of  
124 erosion can be negligible. Preferably the average particle size of fuel additive and carbon based  
125 fuel (coal) is reduced by pulverisation. The additive comprises of oxides or other compounds of  
126 chemical elements from periods 3 and 4 (groups II-V) of the periodic table. The fuel additive  
127 can be injected into the combustion chamber alongside the fuel (preferably in the pulverised fuel  
128 carrying lines) or mixed within the coal based fuel feed. The additive can also replace a  
129 proportion of the carbon based fuel in the amount ranging from 1% to 5% by weight depending  
130 upon the acceptability of the improvement in loss on ignition (LOI) in overall performance  
131 assessment. The coal firing boilers can either produce same steam load by burning less fuel or  
132 increase steam load by burning the same fuel input, depending upon the amount of additive and  
133 improvement in LOI. The fuels used during the experiments included commercially available  
134 coals having low, medium and high ash contents. The Russian sub bituminous medium ash coal,  
135 Columbian low ash coal and UK Kellingley high ash coal (Table 3) were used in the additive  
136 tests.

137

### 138 **3. Results and Discussion**

#### 139 **3.1 Effect on NO emissions**

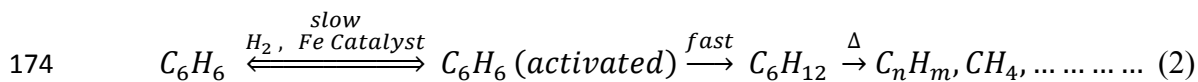
140 Fuel bound nitrogen contributes to about 80% - 95% towards the  $\text{NO}_x$  formation in pulverized  
141 coal combustion while the balance is associated with the thermal and prompt  $\text{NO}_x$ . Fuel bound  
142 nitrogen during coal combustion is generally split into volatile-N and char-N [11]. This division  
143 preferentially depends upon nitrogen content and volatility of coal along with the combustion  
144 conditions such as temperature, residence time, and heating rates [11]. In the case of sub

145 bituminous coals, the volatile-N comprising of tarry compounds decay rapidly to hydrogen  
146 cyanide (HCN) or soot-nitrogen [12-13]. Whereas In contrast the low rank coals would  
147 preferentially release the light nitrogen species such as  $\text{NH}_3$ . Combustion of nitrogenous species  
148 ( $\text{NH}_3$  and HCN) present in the released volatiles and oxidation of the char-nitrogen results in the  
149 formation of oxides of nitrogen. However, the HCN or  $\text{NH}_3$  may also be reduced to  $\text{N}_2$  after  
150 reacting with the available NO. This depends upon the available stoichiometric ratio near the  
151 burner, mixing of the evolved species in the furnace and fuel-N concentration [11-15]. Generally  
152 in-furnace control technologies, air staged combustion and reburning result in less emissions of  
153  $\text{NO}_x$  but at the cost of higher levels of loss on ignition. The oxygen enriched combustion can  
154 facilitate to offset the compromise on loss on ignition [16-19] however, the developed additive is  
155 capable of benefitting not only lower  $\text{NO}_x$  emissions, lower loss on ignition, improved thermal  
156 efficiency and utilise efficiently the fly ash product.

157 Figure 3 shows the effect of addition of both types of Additive towards  $\text{NO}_x$  emissions. The  
158 process of  $\text{NO}_x$  reduction under un-staged combustion observed during additive addition is  
159 associated partly with the interaction of additive fine particles with coal matrix and volatiles as  
160 they are released from coal particles, resulting in cracking of the heavier hydrocarbons favouring  
161 the split of fuel-N into volatile-N (Figure 4). This favours the  $\text{NO}_x$  reduction pathway towards  $\text{N}_2$   
162 formation rather than NO formation by oxidation, since this form of fuel-N is easier to control in  
163 the fuel -rich zones of the flame. This was evident from the fundamental laboratory tests done  
164 (Table 4) on a two stage fixed bed reactor (comprising of two chambers of which one is loaded  
165 with 2-4gms of coal sample pyrolysed with inert gas and the derived gases were reformed in a  
166 second reactor where fuel additive is placed. Products after the second-stage reaction were  
167 condensed by air and dry-ice. The non-condensed gases were collected by the gas sample bag



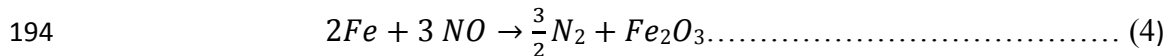
168 and further analysed by gas chromatograph). It has been found that an increase of 33-41% in the  
169 gas yield and 18-47% reduction in tar yield has been established. In literature it has been  
170 reported that tar (of which naphthalene is the main constituent) reduction is controlled by  
171 catalytic decomposition on iron or its oxides. Similarly in case of volatile aromatic  
172 hydrocarbons; benzene, an important intermediate of complex tar reduction mechanism, has been  
173 found to undergo enhanced reduction over iron based catalysts (equation 2) [20-22].



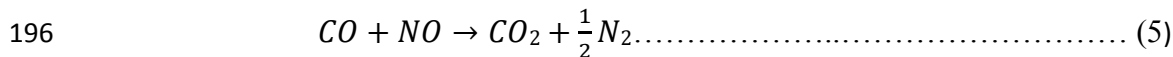
175 Fe-Al catalysts with increase content of iron, increased pore structure and surface area  
176 enhanced the steam reforming of naphthalene. However, the crystalline phase and oxidative  
177 states of the active sites are more influential chemical properties than physical influences [22].  
178 Similarly in a separate study related to pyrolytic cracking of coal tar, the initial heavy tar in the  
179 liquid product decreased by 88% over iron oxide catalyst [23]. However, as part of this study a  
180 range of about 18% to 47% reduction in tar yield was observed compared to RC baseline. This  
181 increase in the gas yield supports the hydrocarbon cracking and release producing more of  
182 volatile which in turn facilitates the NO reduction into N<sub>2</sub> (Figure 4). Moreover, the presence of  
183 iron oxide in the fuel additive would also interact with coal to result in additional NO reduction  
184 reactions supplementing the existing pathway towards N<sub>2</sub> formation. The suggested mechanism  
185 also revolves around the reactions proposed by researchers [24-25]; showing that Fe<sub>2</sub>O<sub>3</sub> can be  
186 reduced to Fe in presence of CO, and later on NO can oxidize iron to reproduce Fe<sub>2</sub>O<sub>3</sub>. In a  
187 separate comprehensive study it has been reported that primarily CO/NO adsorbed on the Fe<sub>2</sub>O<sub>3</sub>  
188 weakens one of the O-Fe bonds by creating a loosely attached O site which further oxidizes CO  
189 to form Fe<sub>2</sub>O<sub>2</sub>. This Fe<sub>2</sub>O<sub>2</sub> now reduces NO via redox (oxidation and reduction steps) reactions

190 to produce oxidized  $Fe_2O_3$  [26]. The interaction amongst CO, NO with additive in the flame  
191 envelope and surrounding region (fuel-rich and fuel-lean pockets) can be summarized as follows;

192



195 The net algebraic addition of reactions yield



197

198 Three different types of coals investigated for the study with a view to observe any  
199 variation in the behaviour of additive on  $NO_x$  reduction. The medium ash Russian Coal (RC)  
200 and high ash Kellingley Coal (KC) resulted in slightly higher reduction in  $NO_x$  as compared  
201 to Columbian Coal (CC) because of relatively higher volatile matter and lower fixed carbon  
202 compared to CC. The air to fuel ratio in the combustion test facility (CTF) was set at 20%  
203 excess air levels (stoichiometric ratio of 1.20) for un-staged flame firing condition. The  
204 optimum range up to 13% by weight of that of coal input was observed for both types of  
205 Additive.  $NO_x$  reduction of 15% & 16% for 13% & 12% mass fractions of WC and AC  
206 Additive were observed for RC, respectively. Whereas, 11% & 10%  $NO_x$  reduction was  
207 achieved for 11% and 13% mass fraction of WC and AC Additive with CC, respectively. KC  
208 with WC and AC Additive co-firing resulted in 14% & 15% reduction in  $NO_x$  for 10% and  
209 13% added mass fractions, respectively. In recent publication it has been found that increasing  
210 the water concentration and temperature of furnace enhances  $Fe_2O_3$  activity during reburning.  
211 It associates with water vapour being an oxidant enhances HCN oxidation to CO and  $N_2$  along  
212 with  $Fe_2O_3$  oxidative ability at high temperature [8].

213 In general the following mechanisms can be summarised towards reduction of NO<sub>x</sub> emissions  
214 using both types of Additive.

- 215 • It is associated partly with the interaction of Additive particles and coal matrix,  
216 resulting in cracking of the heavier hydrocarbons favouring the split of fuel-N into  
217 volatile-N. The increase in the gas yield (Table 4) supported by the higher  
218 concentration of CO and hydrocarbon would favour the NO<sub>x</sub> reduction pathway  
219 towards N<sub>2</sub> formation rather than NO by oxidation, since volatile part of N is easier to  
220 control in the fuel -rich zones of the flame.
- 221 • Additive having higher surface area because of finer particle size distribution  
222 compared to coal, would facilitate the thermal degradation of heavier hydrocarbon into  
223 lighter hydrocarbons and these lighter hydrocarbon are less likely to form Char-N.
- 224 • The presence of iron oxide in the fuel additive would also interact with coal to result  
225 in additional NO<sub>x</sub> reduction reactions supplementing the existing pathway towards N<sub>2</sub>  
226 formation.

227 Figure 5 represents the effect of change of stoichiometric ratio near the combustion zone  
228 on different co-firing blends of Additive with RC, CC and KC. The in-furnace air staged  
229 combustion creates fuel rich zones due to the delayed mixing of fuel particles with air  
230 resulting in the abatement of NO. The reduced stoichiometric ratios i.e. 0.8, 0.9 in primary  
231 combustion zone restrain coal combustion, and a large amount of unburned char enters the  
232 burnout zone resulting in poor carbon burnout. The addition of Additive resulted in an  
233 additional impact on increase in NO reduction with decreasing air to fuel ratio. WC Additive  
234 with RC resulted in a range of 4.6% to 25.8% reduction in NO for range of 0.9 to 1.20  
235 stoichiometric ratio. Whereas, a range of 4.7% to 23.9% was observed for WC/AC Additive

236 with CC for 0.8 to 1.16 changing air to fuel ratios. AC/WC Additive with KC for 0.9 to 1.30  
237 stoichiometric ratio resulted in 7.3% to 31.1% reduction in NO with respect to coal staged  
238 flame base lines.

239

### 240 **3.2 Effect on temperature measurements**

241 The various feed rates of the additive have resulted in increased temperature  
242 measurements close to the burner section; this increase in temperature is due to enhanced and  
243 intensified combustion taking place in the presence of Additive. Figure 6 represents the  
244 temperature differences measured at axial distances downward from the burner with T1 being  
245 close to the burner and T7 near the flue section. The values were calculated for different mass  
246 fractions of additive for all the studied coals against the corresponding coal baseline  
247 temperature measurements. As indicated from the general trend found in Figure 6, the  
248 different mass fraction of Additive produced a broad range of 12-30 °C change in  
249 temperatures at T1. These changes in T1 values are categorically dependent upon the added  
250 mass fraction of Additive. The increase in the temperature also supports the improved values  
251 of loss on ignition. The addition of Additive resulted in generation of extra temperature due to  
252 the burning of the additional carbon of the coal feed, favouring the split of carbon more into  
253 light volatiles rather than remaining in the char.

### 254 **3.3 Effect on Loss on ignition (LOI)**

255 The United States of America, India, China and Australia are the major producers of fly  
256 ash, USA alone produced 57.2 Million metric ton (Mton) of fly ash of which only 22.4 Mton  
257 was used in concrete / cement manufacturing [27]. Fly ash mainly comprising of oxides of  
258 silicon, aluminium and iron principally consists of glassy spheres together with unburnt  
259 carbon and some crystalline matter. The introduction of low NO<sub>x</sub> burners led to a gradual rise

260 in loss on ignition. The unburnt carbon is significant in air-entrained concrete mixtures  
261 because of its tendency of adsorbing air-entrained surfactant rendering less protection against  
262 freeze-thaw conditions. Similarly excessive carbon affects the optimum density and moisture  
263 content for filling applications.

264

265 Additive addition results in a substantial improvement in LOI as evident from Figure 7. The  
266 presence of additive has increased the hydrocarbon intensity and gas yield conversion from  
267 coal, which in turn intensifies the combustion and results in improved LOI. In case of RC, an  
268 overall net reduction for the LOI in the range of 19% to 63% for 1.3% to 13% mass fraction  
269 of added Additive was achieved. Similarly, a range of 20% to 70%; 64% to 70% reductions in  
270 LOI were found for 2.5% to 11%; 5% to 13% mass fractions of added Additive for CC and  
271 KC, respectively. The optimum mass fraction of Additive ranges from 5% to 12% in order to  
272 be used as cement substitute having less than 7% LOI for cement manufacturing. The particle  
273 size distribution (PSD) of resultant coal fly ash can potentially fluctuate depending upon the  
274 operation of the power station. Typically power stations are operated under a steady load to  
275 compensate for variation of the resulting fly ash. General purpose cement utilizes finer ash  
276 because finer the ash the greater the reactivity. Moreover, the variability in the fineness of the  
277 fly ash dictates the strength and water content of resulting concrete. Figure 8 represents  
278 overlay of RC - 4.2% additive resulting fly ash and KC - 4.8% additive fly ash along with RC,  
279 KC and a typical UK fly ash PSD. It can be seen from the graph that with addition of additive  
280 (4.2% to 4.8%) the fineness of resulting fly ash increased by about 36% to 85% in addition to  
281 that of RC and KC fly ash baselines, respectively. This would benefit in terms of improving  
282 the fineness of the resultant fly ash. The addition of additive results in fly ash which falls

283 under PFA BS EN 450 standard where by 40% or less of product fly ash is retained on 45  
284 micron sieve, as well as PFA BS 3892 ( $\leq$  60% retained on 45 microns sieve). Similarly 56  
285 Day cube strength tests on the fly ash of both RC and RC- 4.2% additive mixture were  
286 performed by a major cement manufacturer of the UK. It can be seen from the Table 5 that the  
287 cube strength results are reasonably close to each other without any major variation in the  
288 strength characteristics of the cement mixture. Similarly to comply with Portland cement  
289 requirements,  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  must be above 70% which is true for additive. The addition  
290 of additive has resulted in equally comparable strengthen mortar when prepared by mixing  
291 30% of coal plus additive fly ash blend with Portland cement.

292

### 293 **3.4 Effect on Slagging and Fouling**

294 Slagging and Fouling characterizes the deposits on the radiant section of the boiler and  
295 heat recovery section, respectively. These deposits are formed through a series of complex  
296 mechanism, forming a variety of compounds causing corrosion and reduction in heat transfer  
297 rates. Slagging and fouling indices are used for the assessment of the propensity of fuel ashes  
298 to form these deposits. These indices have been specifically developed for the assessment of  
299 coal ashes only, but these indices are widely used in literature for co-fired fuels as well. Most  
300 commonly used traditional indices used to calculate the fuel ash deposition tendency are  
301 shown in Table 6. The predicted composition is calculated as mass average of the metal  
302 oxides present in the known feed rate of coal and fuel additive. Whereas the actual ash  
303 samples collected during these combustion tests were used to measure the ash components  
304 and were reported as measured values in Table 6. The predicted values of metal oxides are in  
305 close proximity to the actual measured concentration of metal oxides. The existing difference

306 between the values is expected due to the  $\pm 1-2\%$  combined variation in the actual feed rates  
307 of coal and fuel additive. However, irrespective of the predicted and calculated indices, there  
308 is an insignificant increasing trend in both the predicted and measured values of fouling and  
309 slagging indices, when compared with the metal oxide concentration of individual coal fly ash  
310 samples. The reported chemical composition of the fly ash samples show a narrow range of  
311 variety of alkali oxides between coal fly ash and coal fly ash plus fuel additive samples. A  
312 dominance of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  was found in all the fly ash samples. This is partly due to  
313 the inherited concentration of these oxides in the actual coal and fuel additive. The percentage  
314 of oxides of iron was found increased in the fly ash mix, whereas the percentage of alumina  
315 concentration decreased, slightly. Generally substantial increase in the percentage  
316 concentration of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  results in higher fouling propensity in commercial boiler. The  
317 % of  $\text{K}_2\text{O}$  is relatively higher in RC and KC fly ash as compared to Additive; hence addition  
318 of Additive delivers an overall positive impact towards lowering fouling propensities.  
319 Moreover, the tabulated overall measured concentrations show an insignificant variation  
320 concluding trivial effect on the actual boiler furnace wall. Moreover, the measured values of  
321  $R^* \left( \frac{B}{A} \right)$  were less than 0.75 indicating that ash flow temperature will be higher resulting in a  
322 decrease of slagging tendency. The addition of Additive delivers an overall positive impact  
323 towards lowering fouling propensities for the fuels which have relatively higher % of  $\text{Na}_2\text{O}$   
324 and  $\text{K}_2\text{O}$ . It can also result in increasing the ash flow temperature resulting in decrease of  
325 slagging tendency depending on the type of fuel (coal).

326 It is also believed that the use of Additive would cause the passivation of the boiler tubes  
327 (fire side) due to the silicon content of the fuel additive. Albeit, magnetite formed as part of  
328 the passivation process also protects the tube surfaces from further corrosion and it is evident

329 from the Table 1 that both WC and AC Additives contain magnetite forms. It is also  
330 noticeable that the XRD analysis of the KC coal when injected with 10% AC Additive  
331 resulted in 37% of magnetite present in the resultant ash, which again would help with fire  
332 side tube passivation of the boiler. It is also worth mentioning that the XRD analysis also  
333 revealed disappearance of fayalite structure into magnetite which is due to the well-known  
334 interaction of fayalite with generated CO<sub>2</sub> [30].

335 Hence the fuel additive can help on mitigating not only corrosion but also slagging and  
336 fouling issues.

337

338

### 339 **3.5 260 tons/hr MCR commercial boiler results**

340 The burner nozzles of the boiler are positioned to support the tangential projection of  
341 stream of coal plus additive with air to intensify the rapid combustion. Additionally the cavities  
342 of the furnace are up drafted to support carry over the produced fly ash towards electrostatic  
343 precipitators. The installed electrostatic precipitators were able to separate out the product fly ash  
344 along with additive simply because of presence of fayalite and / or magnetite structures,  
345 conducive for conductive properties. Moreover the performance of the precipitators would also  
346 increase due to relatively less unburned carbon present in the product fly ash.

347 The additive was injected via weight in loss feeders (feeding at 2.5tons/hr) in to the coal  
348 mills set at a total coal load of 27.5tons/hr feeding RC. The coal mills load, downstream high  
349 pressure steam manifold and intermediate steam turbine load were all maintained at steady levels  
350 during the overall 6 hours of recorded data. Efficiency improvement though being expressed in  
351 different formats; reported either as absolute or relative change in overall efficiency. The method



352 adopted to report the results for the aforementioned commercial trial is relative change in overall  
353 efficiency adopted from BS EN 12952-15:2003. The calculations based on the measurements  
354 taken from steam, spray water, feed water, coal mass flows at corresponding temperature and  
355 pressure delivered a net 2% improvement in combustion thermal efficiency with added benefit of  
356 9% reduction in NO<sub>x</sub>, 2% increase in steam pressure (Figure 9) with less than 7% unburned  
357 combustible left in fly ash for 9% of added additive. The measured unburned combustibles in  
358 coal fly ash before addition of additive was 12% which reduced down to 7% after additive  
359 injection.

360 The statistical analysis applied to the recorded data produced average, average plus  
361 standard deviation and average minus standard deviation limits. These limits are also highlighted  
362 (red and blue lines) in the Figure 9 for coal and coal plus Additive. The overall induced  
363 fluctuations of steam flow, pressure and NO<sub>x</sub> emissions were found to be with permissible  
364 fluctuations of BS EN 12952-15:2003. Table 7 entails the supporting information regards to the  
365 measured parameter and subsequent calculation employed as per the BS EN 12952-15: 2003. It  
366 is evident that with 2% improvement in combustion efficiency of a 2000 MWe power plant  
367 could result in about £8 Million worth of coal savings with added potential revenue from sales of  
368 high quality fly ash. Hence, the overall viability of this technology is based on return on  
369 investment from fuel savings, NO<sub>x</sub> reduction incentives, and fly ash sales compared to some of  
370 the other alternative technologies (i.e. SNCR, SCR) which partly offer solution for only emission  
371 reductions.

372

## 373 **4 Conclusions**

374 It is evident from the extensive studies performed on lab, pilot and commercial scale that IIT's  
375 commercial Additive is capable of improving combustion thermal efficiency of a full scale  
376 boiler, reducing NO<sub>x</sub> emissions and unburnt carbon in fly ash. The fuel additive is capable of  
377 enhancing the volatile hydrocarbon cracking to facilitate both NO reduction and improved  
378 combustion of coal fired burners as shown in bench scale tests. The overall benefits of the  
379 Additive deliver up to 25% NO reduction, up to 12 °C -30 °C measured increase in the flame  
380 combustion temperatures along with 1%-5% gains in the combustion efficiency depending upon  
381 its injection rates. The optimum range for addition of the fuel additive is within 1% to 12%. The  
382 process also produced fine fly ash with reduced carbon content to levels sufficient for use as  
383 pozzolan. The fuel additive does not adversely affect the slagging and fouling indices by keeping  
384 it below the extremely high range and preferably  $\leq 0.6$  (medium range). The presence of  
385 magnetite and conversion of fayalite to magnetite would also help towards tube side passivation  
386 of the boiler. Hence the Additive addition can help on mitigating not only corrosion but also  
387 slagging and fouling issues.

388

389

### 390 **Acknowledgements**

391 Additive – patented by IIT UK Ltd GB 2462978.

392 We acknowledge the support of analytic team in ETII at the University of Leeds and IIT's due  
393 diligence experts in conducting trials on combustion test facility and 260 tons/hr steam  
394 generating commercial boiler. We would also like to acknowledge the support of the Technology  
395 Strategy Board (TSB) through Knowledge Transfer Partnership (KTP)-008393.

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466  
467

468 **Figure Captions**

469

- 470 1. a: Experimental set up of 100kW combustion test facility, b: Solid state pulverised  
471 additive feeder with vibratory tray, c: Rospen's coal feeder with hopper, screw feeder,  
472 vibratory tray, d: Coal burner with primary air /coal, secondary air, gas flame detector.
- 473 2. Process flow diagram of the commercial boiler (Maximum continuous rating- MCR  $\approx$   
474 270 tons/hr).
- 475 3. Effect of mass fraction of both types of additives on NO emissions from various  
476 commercial coals under un-staged flame conditions of stoichiometric ratio= 1.20; A: WC  
477 Additive with RCl; A': AC Additive with RC; B: WC Additive with CC; B': AC Additive  
478 with CC; C: WC Additive with KC; C': AC Additive with KC.
- 479 4. A: Proposed schematic mechanism for the interaction of the additive with coal [31], B:  
480 NO<sub>x</sub> reduction chemistry pathway [15] in presence of additive, C: Carbon split pathway  
481 in presence of additive.
- 482 5. Effect of stoichiometric ratio on NO emissions from various commercial coals with  
483 varying mass fraction of both types of additives; A-C: 6.4%, 8.8% and 13% mass fraction  
484 of WC Additive with RC; D-F: 5.45%, 6.2% and 7.8% mass fraction of WC, AC and WC  
485 Additive with CC, respectively; G-I: 8.9%, 9.1% and 10.3% mass fraction of AC, WC  
486 and AC with KC, respectively.
- 487 6. Temperature measurements for different mass fraction of Additive A: RC with additive;  
488 B: CC with additive; C: KC with additive.
- 489 7. LOI versus mass fraction of additive A: Russian coal; B: Columbian coal; C: Kellingley  
490 coal.
- 491 8. PSD comparison between coal fly ash with and without additive.
- 492 9. Recorded parameters during the trial on 260 tons/hr boiler (NO<sub>x</sub>, Steam pressure, Steam  
493 flow).

494

495 **Table captions**

- 496 1. XRF / XRD composition of Water and Air Cooled Additive Overall oxygen  
497 concentration in the combustion air.
- 498 2. Particle size distribution, physical and chemical properties of the Additive.
- 499 3. Chemical composition of tested coals.
- 500 4. Gas / Oil yields and concentration of gases.
- 501 5. Compressive strength tests on Russian coal fly ash with and without additive
- 502 6. Calculated and predicted slagging and fouling indices
- 503 7. Boiler efficiency calculations with and without additive
- 504
- 505

**Nomenclature:**

<b>Description</b>	<b>Symbols and corresponding units</b>
Main steam flow	$m_{ST}$ , kg/s
Specific enthalpy of main steam	$h_{ST}$ , kJ/kg
Spray water flow rate to the main steam at temperature	$m_{SS}$ , kg/s
Specific enthalpy of spray water	$h_{SS}$ , kJ/kg
Boiler feed water flow rate	$m_{FW}$ , kg/s
Specific enthalpy of spray water	$h_{FW}$ , kJ/kg
Total coal flow to the boiler-6	$m_F$ , kg/s
NCV of the coal	$H_{(N)}$ , kJ/kg
Specific heat of the fuel	$C_F$ , kJ/kg-°C
Average temperature of the coal supply (fuel)	$t_F$ , °C
Reference temperature	$t_r$ , 25 °C
Specific heat of the air	$C_{PA}$ , kJ/kg-°C
Combustion air to mass fuel ratio	$\mu_A$ , kg/kg
Ratio of unburned to supplied fuel mass flows	$l_u$
Ash content in the fuel	$\gamma_{Ash}$ , kg/kg
Moisture content in the fuel	$\gamma_{H_2O}$ , kg/kg
Volatile matter content of ash	$v$ , kg/kg
Unburned combustible content of slag	$u_{SL}$ , kg/kg
Ratio of collected furnace bottom-ash mass to mass of ash in fuel minus its volatile fraction	$\eta_{SL} = 0.05$
Unburned combustible content of fly ash	$u_{FA}$ , kg/kg
Fly ash retention efficiency	$\eta_{FA} = 0.95$



Coal Pulveriser power	$P_M, \text{ kW}$
Any other power required on motors	$P, \text{ kW}$
Average temperature of the flue gas	$t_G, ^\circ\text{C}$
Useful heat output	$Q_N, \text{ kW}$
Total heat input	$Q_{(N)Ztot}, \text{ kW}$
Thermal efficiency by Direct method	$\eta (N)B$