

**MODELLING PRIMARY NO<sub>x</sub> AND PRIMARY N<sub>2</sub>O OF PULVERISED FUEL COMBUSTION (PFC) AND CIRCULATING FLUIDISED BED COMBUSTION (CFBC)**

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**Abstract** – With more stringent emissions limits with time, including NO<sub>x</sub> and N<sub>2</sub>O, and due to the high costs of secondary measures for NO<sub>x</sub> emissions reduction, knowledge of primary NO<sub>x</sub> and primary N<sub>2</sub>O is very important. With this knowledge primary NO<sub>x</sub> and primary N<sub>2</sub>O can be reduced at low costs and in this way the costs for secondary measures are much reduced as well.

In this paper, mathematical models regarding primary NO<sub>x</sub> of PFC, and primary NO<sub>x</sub> and primary N<sub>2</sub>O of CFBC are presented. The models are based on data from large-scale power stations. With CFBC the models hold for the fuels coal, lignite and wood only, and not for co-combustion. This paper presents a part of a much larger study regarding this subject.

The models as developed are:

PFC, NO<sub>x</sub>, eq. 2:

$$NO_x = (NO_p + NO_p \times f_1 \times N \times FR) \times \text{Lambda}$$

CFBC, NO<sub>x</sub>, eq. 5:

$$NO_x = \frac{C2 \times \text{Lambda}^2 \times N \times \exp\left(\frac{-3215}{\text{Temperature}}\right)}{(FR + 1)^{0.8}}$$

CBCF, N<sub>2</sub>O, eq. 6:

$$N_2O = C3 \times \text{Lambda}^{4.4} \times N \times FR^{0.8} \times \exp\left(\frac{8100}{\text{Temperature}}\right)$$

With N as N-content of the fuel in g/GJ (LHV), Lambda as the air to fuel ratio, FR as the fuel ratio, Temperature in K, NO<sub>x</sub> and NO<sub>p</sub> as NO<sub>2</sub> in mg/Nm<sup>3</sup>, dry and at 6vol.% O<sub>2</sub>, N<sub>2</sub>O in mg/Nm<sup>3</sup>, dry and at 6vol.% O<sub>2</sub>, f<sub>1</sub>, C2 and C3 as constants, which depend on the furnace, and NO<sub>p</sub> as primary thermal NO<sub>x</sub>, which also depends on the furnace.

Modelling of primary NO<sub>x</sub> with PFC and CFBC is not new. Modelling of primary N<sub>2</sub>O with CFBC is not new. With increasing temperature, primary N<sub>2</sub>O reduces. With PFC, primary NO<sub>x</sub> is about formation only. With CFBC, primary NO<sub>x</sub> and primary N<sub>2</sub>O are about formation and reduction.

From a qualitative point of view, the mathematical models of primary NO<sub>x</sub> are useful, both with PFC and CFBC. From a quantitative point of view, the models of primary NO<sub>x</sub> with CFBC and PFC, and N<sub>2</sub>O with CFBC, are not satisfactory. They hold for a specific boiler only. Primary emissions of NO<sub>x</sub> and N<sub>2</sub>O of CFBC also depend on air staging, catalytic activity of the ash and/or bed material, the bed inventory, “limestone addition”, cyclone separation efficiency, flue gas residence time, etcetera, which are not (yet) modelled. In this paper attention is paid to the CFBC design parameters cyclone separation efficiency, limestone addition and the height of the secondary air ports above the bottom, and their influence on primary NO<sub>x</sub> and -N<sub>2</sub>O. These design

parameters easily explain for the variations of primary NO<sub>x</sub> and primary N<sub>2</sub>O emissions encountered and modelled.

The presence of catalytically active elements, like Na, K, Fe, Mg and Ca, in the fuel, the ash and the bed material must be considered as well, which is often not the case in literature. For instance wood is usually rich in K and Ca, and lignite can be rich in Ca. This also means: where there are rules, there are exceptions as well.

The addition of limestone to the bed can increase primary NO<sub>x</sub> drastically, depending on the fuel, and hence in such cases limestone addition is definitely a bad idea.

There is room for further research regarding both mathematical- and CFD modelling of primary NO<sub>x</sub> and -N<sub>2</sub>O with CFBC, amongst others regarding the effect of increasing Lambda on primary N<sub>2</sub>O and its cause, the presence of thermal NO<sub>x</sub> or not, co-combustion and other “fuels”, like pet coles and dried municipal sewage sludge.

## INTRODUCTION

Emissions of NO<sub>x</sub> are an important subject for both types of power stations, PFC and CFBC. With time, more attention is paid to reduction of NO<sub>x</sub> emissions, using both primary and secondary measures, as the emission limits become more stringent with time. Reduction of NO<sub>x</sub> emissions is accompanied with large risks and high costs.

This paper is limited to firing solid fuels, and to PFC and CFBC. This paper is part of a more extended study regarding PFC, CFBC, primary NO<sub>x</sub> and primary N<sub>2</sub>O.

Primary measures are relatively economic, compared to secondary measures like S(N)CR. So, prediction of primary NO<sub>x</sub> is important, for instance when considering a fuel switch, installation of new low-NO<sub>x</sub> burners, changing operating parameters, etcetera.

Emissions of N<sub>2</sub>O are also an important subject, as N<sub>2</sub>O is a strong greenhouse gas and causes depletion of the ozone layer. For this paper, the N<sub>2</sub>O emissions are only relevant with CFBC. With CFBC, emissions of N<sub>2</sub>O are limited by increasing the combustion temperature to > 900°C (but not for wood-firing), which also means abandoning in-bed flue gas desulphurisation (van Dijen, 2010).

In the past, extensive studies have been published regarding the formation of N<sub>2</sub>O and NO<sub>x</sub> with firing coal and lignite (VGB, 1994; Pels, 1995; Zelkowsky, 2004). Attention especially focussed on CFBC and FBC. In the past extensive studies were performed regarding low NO<sub>x</sub> combustion with PFC, especially the design of burners, staged combustion and flue gas recirculation. These studies did not result in mathematical models. However, with PFC, high quality CFD models are available, for instance from the company Recom Services. With CFBC, high quality CFD models are also available, for instance from the company Aix Process and the company VTT. Their models include primary NO<sub>x</sub> (and N<sub>2</sub>O), but the quality of the CFD CFBC models regarding NO<sub>x</sub> and N<sub>2</sub>O is still very limited.

## PFC AND PRIMARY NO<sub>x</sub>

Attention was paid to modelling and prediction of primary NO<sub>x</sub> of PFC, based on data obtained from a KEMA thesis (van Dijen, 2002; Rozendaal, 1999). With a combustion temperature of 1400°C and more, thermal NO<sub>x</sub> is important with PFC.

There are at least 4 important aspects:

- The specific N-content of the fuel, expressed in g/GJ<sub>fuel</sub>. This GJ<sub>fuel</sub> is based on the LHV.
- The value of the FR of the fuel.
- The value of Lambda.
- The furnace. This for instance means the type of burners, the air (primary-, secondary-, overfire-, wall-air), the O<sub>2</sub> content of the flue gases, the residence time of flue gases and fuel, the quality of mixing of air and fuel, the particle size distribution of the fuel, etcetera.

With modern PFC power stations, the O<sub>2</sub> content of the flue gases is about 3vol.%. With increasing O<sub>2</sub> content, the thermal NO<sub>x</sub> will increase. However, the combustion temperature will be reduced, resulting in less thermal NO<sub>x</sub>. In general, primary NO<sub>x</sub> will increase with increasing O<sub>2</sub> content.

The formula used for modelling primary NO<sub>x</sub> is:

$$NO_x = NO_p + NO_p \times f1 \times N \times FR \quad (1)$$

With:

- NO<sub>x</sub> as primary NO<sub>x</sub> as NO<sub>2</sub> in mg/Nm<sup>3</sup>, dry and at 6vol.% O<sub>2</sub>
- NO<sub>p</sub> as primary NO<sub>x</sub> as NO<sub>2</sub>, dry and at 6vol.% O<sub>2</sub>, when the fuel does not contain N. NO<sub>p</sub> depends on the furnace.
- FR as fuel ratio, which is the ratio fixed carbon / volatile matter, in the same units
- N as the nitrogen content of the fuel in g/GJ (LHV)
- f1 as a factor, which depends on the furnace, and which can be for example 1.25 x 10<sup>-3</sup>.

NO<sub>p</sub> is the first term and presents the thermal NO<sub>x</sub>. The second term is the fuel NO<sub>x</sub>. This second term indicates, that when either fuel-N is zero or FR is zero, fuel NO<sub>x</sub> is zero is well.

With modern low-NO<sub>x</sub> technology, primary NO<sub>x</sub> varies between 300 and 600mg/Nm<sup>3</sup>, dry and at 6vol.% O<sub>2</sub>, as NO<sub>2</sub>. Even lower values are reported, as indicated below. These emissions depend on the fuel as well, as indicated above.

With PFC, primary NO<sub>x</sub> is about 95vol.% NO and maximum 5vol.% NO<sub>2</sub>. With firing hard-coal, thermal NO<sub>x</sub> can be 200mg/Nm<sup>3</sup> and fuel-NO<sub>x</sub> can be also 200mg/Nm<sup>3</sup>, resulting in total, primary NO<sub>x</sub> of 400mg/Nm<sup>3</sup>, dry and at 6vol.% O<sub>2</sub>. With firing bituminous coal, the company RJM International claims primary NO<sub>x</sub> emissions of about 250mg/Nm<sup>3</sup>, dry and at 6vol.% O<sub>2</sub>, as NO<sub>2</sub> (Riley, 2016). This with “low” emissions of CO, low UBC in ash and absence of CO corrosion, it is claimed (Riley, 2016).

This modelling has proved its value with fuels such as coal, pet cokes, lignite, dry municipal sewage sludge and wood. It also proved its value with co-combustion.

The formula used for modelling primary NO<sub>x</sub> could be modified like:

$$NO_x = NO_p \times \text{Lambda}^a + NO_p \times f1 \times N \times FR$$

or:

$$NO_x = (NO_p + NO_p \times f1 \times N \times FR) \times \text{Lambda} \quad (2)$$

This for a small variation (1.0 to 1.4) of Lambda, which is the air to fuel ratio, see figures 1 and 2. The value of “a” could be about 1 to 2. Obviously the values of NO<sub>p</sub> must be adapted, see the 2 example calculations below. NO<sub>p</sub> as primary NO<sub>x</sub> as NO<sub>2</sub>, dry and at 6vol.% O<sub>2</sub>, when the fuel does not contain N and corrected for the value of Lambda, which means extrapolated for Lambda = 1. At high values of Lambda of > 1.4, the value of NO<sub>x</sub> decreases, because the combustion temperature decreases. Eq. 2 is now an equation with 4 important aspects: N-content of the fuel, FR of the fuel, Lambda and the furnace.

The model is applied and confirmed within the company ENGIE, with firing bituminous coal and dry wood, and with co-firing bituminous coal with dry wood or with dry municipal sewage sludge.

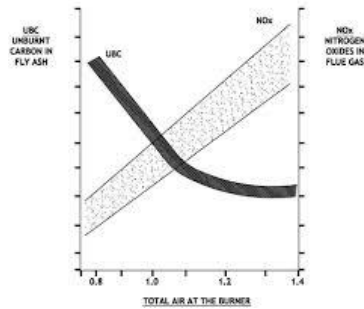


Fig. 1: NOx and excess air (Lambda > 1).

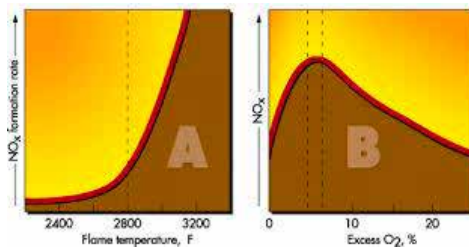


Fig. 2: NOx and excess air.

Calculation examples:

Eq. 1:

$$\text{NOx} = 200 + 200 \times 1.25 \times 10^{-3} \times 400 \times 2.0 = 200 + 200 = 400 \text{ mg/Nm}^3, \text{ dry and at 6vol.\% O}_2, \text{ as NO}_2$$

Eq. 2:

$$\text{NOx} = (171 + 171 \times 1.25 \times 10^{-3} \times 400 \times 2.0) \times 1.17 = (171 + 171) \times 1.17 = 400 \text{ mg/Nm}^3, \text{ dry and at 6vol.\% O}_2, \text{ as NO}_2$$

### CFBC AND PRIMARY NOx

Modelling primary NOx with CFBC proved to be more complex, compared to PFC. Disagreement between the different sources can be encountered in literature, on subjects like whether thermal NOx is relevant at combustion temperatures of about 850°C, or not. So, according to literature, the part of thermal NOx in primary NOx with CFBC may vary between 0 and 25%, when firing hard-coal. Of course, this means that fuel-NOx may vary between 75 and 100%. When thermal NOx is present, it can originate from local hot spots. (Oka (2004) indicates, that the temperature of char particles is significantly higher than the bed temperature, by about 50 to 200°C.

Advantages of CFBC over PFC regarding NOx are:

- Lower primary NOx, with about 200mg/Nm<sup>3</sup> for hard-coal, as NO<sub>2</sub>, dry and at 6vol.% O<sub>2</sub>
- SNCR is easily applied.

A disadvantage of CFBC over PFC regarding N<sub>2</sub>O is:

- Formation of N<sub>2</sub>O at temperatures below about 950°C must be considered, except for wood-firing, see also below.

The bed material, which is usually ash, and/or the limestone added to the bed for in-bed flue gas desulphurisation, can act as catalyst, both for the formation of NO<sub>x</sub> and for the reduction of NO<sub>x</sub>, at least according to literature. UBC can result in reduction of NO<sub>x</sub>, and UBC depends amongst others on the FR of the fuel. According to literature, CO in the flue gases may reduce NO<sub>x</sub>. However, this is denied in literature as well. Besides, also with CFBC not all furnaces are the same, regarding combustion temperature, O<sub>2</sub> content of the flue gases, mixing of fuel and air, the air itself (primary, secondary, tertiary), the height of the secondary air ports above the bottom, the relative amount of bed material, the quality of bed material, cyclones separation efficiency, limestone addition, flue gas residence time, etcetera.

With modern CFBC power stations, the O<sub>2</sub> content of the flue gases is about 3vol.%. The combustion temperature usually varies between 800 and 950°C. A combustion of about 850°C is considered as optimum for both combustion and in-bed flue gas desulphurisation. The combustion temperature varies somewhat with the position in the furnace. With increasing temperature, the combustion improves but flue gas desulphurisation becomes worse.

NO<sub>x</sub>, excluding N<sub>2</sub>O, increases with increasing temperature (Basu, 2006). According to me, this seems less related to thermal NO<sub>x</sub> and more to better combustion with increasing temperature: less UBC and less CO are present (Xiao, 2005). Besides, thermal NO<sub>x</sub> is anticipated only at temperatures higher than about 1400°C. NO<sub>x</sub>, including N<sub>2</sub>O, remains stable with increasing temperature (Basu, 2006). Primary NO<sub>x</sub> also increases with increasing O<sub>2</sub> content of the flue gases (Basu, 2006). This seems also related to better combustion: less UBC and less CO are present (Xiao, 2005). It is also indicated, that a low FR results in more NO<sub>x</sub>, and less N<sub>2</sub>O (Oka, 2004).

Recently new literature appeared regarding primary NO<sub>x</sub> of CFBC, including modelling (Jingji, 2015). However, this modelling should be improved, as it deviates from established physical and chemical aspects of NO<sub>x</sub> formation. However, it has a good database, regarding hard-coal firing. The NO<sub>x</sub> emissions originate from full-scale CFBCs. It is important to use data from full-scale CFBC's, as the data and results deviate from those obtained with small-scale and laboratory CFBC's (Zhou, 2013). The database from (Jingji, 2015) regarding the coals is presented in table 1. The last 2 columns are added by me. Table 2 contains additions from me, especially considering other fuels. Part of this data comes from van Dijen (2013) and VGB (1992).

Table 1: Results of coal analyses, as received, including FC. VM as dry and ash free (Jingji, 2015). M means moisture, A means ash, FC means fixed carbon, VM means volatile matter, FR means fuel ratio and N means nitrogen content.

	C	H	O	N	S	M	A	FC	VM	LHV	FR	N
Unit	wt.%									MJ/kg	-	g/GJ (LHV)
Chengfeng	38.18	2.26	3.08	0.34	0.34	7.5	48.31	33.23	24.80	14.09	3.0	241
Lvchang	41.81	2.36	4.16	0.57	0.45	5.85	44.71	33.25	32.75	15.07	2.1	378
Fengxi	62.53	3.39	5.12	0.67	0.41	12.22	15.65	47.06	34.76	23.46	1.9	286
Xinlianxin	58.48	3.00	4.20	0.57	0.49	15.24	18.11	48.57	27.13	21.60	2.7	264
Dongming	40.64	2.61	3.26	0.69	0.80	8.33	43.67	29.00	39.57	15.03	1.5	459
Hongda	39.84	2.63	4.19	0.67	0.65	8.74	43.29	26.66	44.43	14.34	1.3	467
Runze	47.21	2.76	3.74	0.38	0.49	6.69	38.74	36.37	33.34	17.48	2.0	217
Binneng	46.28	3.00	8.21	0.54	0.46	14.54	26.97	36.00	38.45	18.05	1.6	299
Huanggu	33.89	2.42	6.79	0.32	1.07	11.12	44.38	23.37	47.48	13.23	1.1	242
Jin'an	41.59	2.66	11.01	0.53	0.16	32.22	11.83	30.44	45.60	15.67	1.2	338
Darkai	39.80	2.39	12.01	0.49	0.19	36.92	8.21	29.98	45.36	14.73	1.2	333
Yushu	40.75	2.67	10.17	0.61	0.32	31.92	13.55	29.71	45.51	15.29	1.2	399
Yuanguan	33.07	2.41	9.67	0.43	0.62	30.84	22.96	24.34	47.32	12.75	1.1	337
Yuguang	36.59	2.68	10.68	0.25	1.45	11.52	36.82	30.56	40.84	14.88	1.4	168
Zongneng	46.16	3.13	7.64	0.47	0.72	11.08	30.80	32.64	43.84	16.95	1.3	277

Table 2: Results of fuel analyses, as received, including FC. VM as dry and ash free. M means moisture, A means ash, FC means fixed carbon, VM means volatile matter, FR means fuel ratio and N means nitrogen content.

	C	H	O	N	S	M	A	FC	VM	LHV	FR	N
Unit	wt.%									MJ/kg	-	g/GJ (LHV)
Polaniec Wet wood chips + 20wt.% PKS	29	3.5	25.5	0.114	0.02	42	0.3	12	80	11.1	0.25	103
(14 V-27)												
Coal 1	65.5	4.3	13.0	0.95	1.07	9.4	5.7	52.5	38.2	28.5*	1.6	333
Coal 2	66.4	4.2	9.4	1.22	0.82	10.6	7.3	50.9	38.0	27.9*	1.6	437
Coal 3	49.1	3.5	6.8	0.79	1.32	5.7	32.7	36.5	40.8	20.9*	1.45	378
Coal 4	48.8	3.4	6.6	0.65	1.05	4.3	35.2	36.5	39.6	20.6*	1.5	316
Lignite 1**	61*	4.4*	20*	0.8*	0.4*	11	4	38.2	55	21.2	0.8	377
(14 V-28)												
Coal 1	67.3	4.3	5.2	1.35	1.43	11.0	9.4	53.3	33.0	27.9	2.0	484
Coal 2	68.1	4.3	7.9	1.15	0.58	8.8	9.3	53.5	34.7	27.7	1.9	415
Peat	29.2	3.2	18.7	0.78	0.21	43.0	4.8	19.6	62.4	10.8	0.60	722
Wood chips***	26.8	3.2	22.0	0.26	0.016	46.1	1.6	12.1	76.8	9.7	0.30	268
(14 V-33)												
Coal 1	77.7	3.6	3.2	1.48	0.72	6.9	6.3	75.3	13.2	29.9	6.6	495

\*Estimated by me. \*\*Obviously this is dried lignite. \*\*\*Including branches, twigs and needles.

Table 2 indicates that a mixture of wet wood chips and palm kernel shells was fired. From a chemical point of view palm kernel shells are like wood, but the N-content is about 0.45wt.% and the LHV is about 17.9MJ/kg, as it contains about 10wt.% moisture.

Comparing wood with bituminous coals, the ash content, the FR and the N content are very low. (Quartz) sand is often used as bed material, resulting in “fly ash” with low content of UBC. Comparing lignite with bituminous coals, the ash content and the FR are low.

In table 3, which is related to table 1, the data of the units is presented (Jingji, 2015). Lambda is the ratio of air to fuel. V (the specific flue gas Volume) is introduced to keep the dimension unity in the correlation.

Table 3: Data of the Chinese units (Jingji, 2015). UBC means in fly ash, as mass fraction. NOx as NO<sub>2</sub> is dry and at 6vol.% O<sub>2</sub>. V is the dry flue gas volume per unit weight fuel at 6vol.% O<sub>2</sub>.

	Test	V	UBC	Temperature	Lambda	NOx
Unit	-	Nm <sup>3</sup> /kg	-	K	-	mg/Nm <sup>3</sup>
Chengfeng	3	5.36	0.1327	1188	1.51	216
	6	5.36	0.1327	1128	1.22	94
Lvchang	10	5.82	0.1052	1196	1.30	118
Fengxi	4	8.67	0.2321	1151	1.5	111
Xinlianxin	1	8.08	0.0169	1160	1.34	159
Dongming	4	5.79	0.0374	1195	2.01	550
	6	5.79	0.0374	1201	1.73	387
Hongda	1	5.65	0.0735	1202	1.34	203
Runze	3	6.62	0.0399	1219	1.44	238
Binneng	1	6.40	0.0252	1216	1.25	233
	2	6.40	0.0047	1221	1.21	277

Huanggu	2	4.76	0.0245	1234	1.35	304
	3	4.76	0.0245	1212	1.29	447
	4	4.76	0.0245	1263	1.44	539
Jin'an	3	5.59	0.057	1145	1.18	313
Darkai	1-3	5.24	0.0241	1240	1.35	347
	1-5	5.24	0.0241	1225	1.41	369
	1-6	5.24	0.0241	1210	1.24	249
	2-1	5.24	0.0241	1206	1.21	244
	2-2	5.24	0.0241	1215	1.09	197
Yushu	3	5.53	0.0066	1107	1.35	302
Yuanguyuan	3	4.52	0.0128	1149	1.31	398
	6	4.52	0.0128	1075	1.10	212
Yuguang	7	5.04	0.0411	1087	1.27	184
Zongneng	1	6.46	0.0100	1098	1.24	258

In table 4, which is related to table 2, the data of other units is presented. When firing other wood chips (with palm kernel shells) in the Polaniec unit, probably wood chips with a higher specific N-content, primary NO<sub>x</sub> is about 180mg/Nm<sup>3</sup>. The Polaniec example presented is with wood chips with a very low specific N-content.

With table 4, V is calculated as (VGB, 2012):  $V = LHV \times 0.359$ , with 0.359 in Nm<sup>3</sup>/MJ (LHV).

Table 4: Data of the units. UBC means in fly ash, as mass fraction. N<sub>2</sub>O and NO<sub>x</sub> as NO<sub>2</sub> are dry and at 6vol.% O<sub>2</sub>. V is the dry flue gas volume per unit weight fuel at 6vol.% O<sub>2</sub>.

	Test	V	UB C	Temperature	Lambda	NO <sub>x</sub>	N <sub>2</sub> O
Unit	-	Nm <sup>3</sup> /kg	-	K	-	mg/Nm <sup>3</sup>	
Polaniec	Wet wood chips	4.00		1123	1.25	120	4
(14 V-27) Pforzheim	Coal 1	10.26	-	1073 to 1173	1.05 to 1.4	50 to 250	60 to 400
	Coal 2	10.04	-	1073 to 1143	ca. 1.2	60 to 100	170 to 260
	Coal 4	7.42	-	1043 to 1103	ca. 1.2	20 to 30	240 to 340
Saarbrücken	Coal 3	7.52	-	1053 to 1193	1.1 to 1.4	100 to 240	20 to 260
	Coal 4	7.42	-	1053 to 1193	1.1 to 1.4	50 to 110	20 to 260
Cologne	Lignite 1	7.63	-	1013 to 1193	1.05 to 1.5	40 to 280	2 to 32
(14 V-28) Orebro	Coal 1	10.04	-	1098 to 1178	1.27	20 to 150	60 to 160
	Coal 2	9.97	-	1088 to 1148	1.25 to 1.45	30 to 90	70 to 120
	Peat	3.89	-	1073 to 1133	1.15 to 1.4	30 to 60	50 to 110
	Wood chips	3.49	-	1088	1.25 to 1.45	60 to 110	20
(14 V-33) Leverkusen	Coal 1	10.76	-	1123 to 1173	1.1 to 1.35	25 to 50	-

The correlations proposed are (Jingji, 2015):

$$NO_x = \frac{8635.4 \times VM^{0.5934} \times Lambda^{2.0641} \times \exp\left(\frac{-3215.4}{Temperature}\right)}{V \times UBC^{0.2441}} \quad (3)$$

$$NOx = \frac{38174 \times VM^{0.8375} \times \text{Lambda}^{2.0641} \times \exp\left(\frac{-3215.4}{\text{Temperature}}\right)}{V^{1.2441}} \quad (3)$$

With Temperature as bed temperature in K, UBC as mass fraction carbon in fly ash, Lambda as air to fuel ratio (and not excess air), VM as volatile matter dry and ash free and in wt.%, V as standard flue gas volume per unit weight of fuel in Nm<sup>3</sup>/kg (dry and at 6vol.% O<sub>2</sub>), NOx as concentration in mg/Nm<sup>3</sup> (as NO<sub>2</sub>, dry and at 6vol.% O<sub>2</sub>).

These correlations indicate that primary NOx:

- Increases with increasing temperature, based on an Arrhenius equation
- Increases with increasing Lambda, which also means increasing excess air
- Increases with increasing VM, which means decreases with increasing fuel ratio FR
- Decreases with increasing UBC in the fly ash
- Decreases with increasing V
- Does not depend on the N-content of the fuel.

According to me, it is better to replace VM with FR, as often VM (dry and ash free), VM (as received) and/or VM (dry) are mixed up. Besides, VM as received depends on the ash content and the moisture content, whereas FR as received, dry, or dry and ash free, is independent of ash content and moisture content of the fuel. There is no physical or chemical reason, why only VM must be considered, and not FC as well, on the contrary. It seems not logical to have no influence of the N-content of the fuel, because when the N-content of the fuel would be zero, there would not / hardly be any primary NOx. Much of the literature on formation of NOx and N<sub>2</sub>O considers the N-content of the fuel, see for instance (van Dijen, 2002; Rozendaal, 1999; Cai, 2015; Bernhardt, 2015). It is suggested that UBC x VM = 0.00227 x V (Jingji, 2015). This correlation probably comes from: UBC = 0.84 x LHV/VM and LHV = 0.0027 x V (Jingji, 2015). The V seems without a physical or chemical meaning. It also seems illogical that UBC increases with the increasing LHV. It is well known, that with the usual solid fuels, 1 GJ (LHV) results in 300Nm<sup>3</sup> of flue gas, dry and at 3vol.% O<sub>2</sub>, and in 359Nm<sup>3</sup> of flue gas, dry and at 6vol.% O<sub>2</sub> (VGB, 2012). UBC does not only depend on the combustion and the FR, but also on the ash content of the fuel. V also depends on the ash content of the fuel.

The correlation of UBC x VM = 0.00227 x V suggests, that when VM is high, UBC is low, for a constant value of V. In other words, UBC is low when FR is low.

So, I suggest to use correlations like:

$$NOx = \frac{C1 \times \text{Lambda}^b \times N^d \times \exp\left(\frac{-3215.4}{\text{Temperature}}\right)}{(FR+1)^a \times UBC^c} \quad (4)$$

$$NOx = \frac{C2 \times \text{Lambda}^b \times N^d \times \exp\left(\frac{-3215.4}{\text{Temperature}}\right)}{(FR+1)^e} \quad (4)$$

With N as nitrogen content in g/GJ, and C1 and C2 as constants. The dimension analyses indicate, that a factor with dimension Nm<sup>3</sup>/GJ must be added to the correlations, which is the 359Nm<sup>3</sup>/GJ mentioned above (VGB, 2012). So, the dimensions of C1 and C2 become Nm<sup>3</sup>/GJ. VM is replaced by 1/(FR + 1), as FR = FC/VM = (1 - VM)/VM = 1/VM - 1. Here VM is in mass fraction, dry and ash free. FC is also in mass fraction, dry and ash free.

These correlations can be partially copied from previous correlations, and simplified:

$$NOx = \frac{C1 \times \text{Lambda}^2 \times N^d \times \exp\left(\frac{-3215}{\text{Temperature}}\right)}{(FR+1)^a \times UBC^{0.25}} \quad (5)$$

$$NOx = \frac{C2 \times \text{Lambda}^2 \times N^d \times \exp\left(\frac{-3215}{\text{Temperature}}\right)}{(FR+1)^{0.8}} \quad (5)$$



Table 5 presents the values of C2, as calculated with equation 5, for  $d = 1$ . Which value of  $d$  is correct? Reference (VGB, 1992, 14 V-27) suggests that NOx emissions are clearly increased with increasing specific N-content of the coal. The FRs of both coals (2 and 4) are similar. Reference (VGB, 1992, 14 V-28) is not clear regarding the increase or decrease of NOx emissions with increasing specific N-content of the coal. The FRs of both coals are similar.

Table 5: Calculated values for C2, with  $d = 1$  ( $= N^1$ ).

Unit	Test	C2	Unit	Test	C2
Chengfeng	3	17.9	Polaniec	Wet wood chips	15
	6	13.7			
Lvchang	10	6.72	Pforzheim	Coal 1	6.1
				Coal 2	5.4
				Coal 4	3.2
Fengxi	4	6.6	Saarbrücken	Coal 4	5.2
Xinlianxin	1	15.2	Cologne	Lignite 1	5.2
Dongming	4	9.1	Orebro	Coal 1	2.7
	6	8.6		Coal 2	3.1
				Wood chips	3.8
Hongda	1	6.84	Leverkusen	Coal 1	3.4
Runze	3	17.8			
Binneng	1	15.1			
	2	17.7			
Huanggu	2	16.9			
	3	28.5			
	4	24.8			
Jin'an	3	20.7			
Darkai	1-3	14.4			
	1-5	14.7			
	1-6	13.0			
	2-1	13.5			
	2-2	13.2			
Yushu	3	14.3			
Yuangyuan	3	20.5			
	6	18.7			
Yuguang	7	26			
Zongneng	1	22.0			

Table 5 strongly suggests that the value of C2 depends on the unit. The factor C2 varies with a factor 4, depending on the unit! In table 5, the case Huanggu 2 seems an exception. On average, the values of the units of the right part of the table are much less than the values of the units of the left part of the table 5, obviously with a few exceptions. Possibly this difference is related to:

- A different ratio of primary to secondary air
- The height of the secondary air ports above the bottom
- The cyclone separation efficiency
- Flue gas residence time

- “Limestone addition”
- Etcetera.

Depending on the data set used, other values for a, d, C1, the exponential value and C2 can be found (14). For instance:

- An exponential value of -14000 or -15000 (K), instead of -3215.
- $\Lambda^4$ , instead of  $\Lambda^2$ .

These correlations assume there is fuel-NO<sub>x</sub> only, as when N = 0, NO<sub>x</sub> = 0 as well. As large-scale CFBC units are not identical, the factors C1 and C2 should depend on the unit, more or less (VGB, 1992). Besides, aspects such as catalytic effects of ashes, lime/CaSO<sub>4</sub>, bed material, ratio of primary to secondary air, cyclone separation efficiency, flue gas residence time, etcetera, are not included in the model. The use of (FR+1), instead of FR, means that NO<sub>x</sub> is not extremely high with fuels with FR = 0, like with gaseous fuels, many liquid fuels, and some (waste) polymers.

Especially the presence of a high-efficiency cyclone or high-efficiency cyclones is important, for reducing the UBC content of the fly ash (Xiao, 2005), and of course, keeping the bed inventory.

### CFBC AND N<sub>2</sub>O

Formation of N<sub>2</sub>O with thermal power stations has been extensively studied in the past (VGB, 1994). With PFC, the emissions of N<sub>2</sub>O are neglected, which is related to the high combustion temperature of about 1400°C and more (VGB, 1994).

With CFBC, emissions of N<sub>2</sub>O are an issue at combustion temperatures below about 950°C (Basu, 2006; van Dijken, 2013). A low FR of the fuel results in less N<sub>2</sub>O. A low N-content of the fuel, expressed as g/GJ, results in less N<sub>2</sub>O (van Dijken, 2013). N<sub>2</sub>O increases with increasing value of  $\Lambda$  (van Dijken, 2013).

A correlation regarding N<sub>2</sub>O emissions could be:

$$N_2O = C3 \times FR^a \times N^b \times \Lambda^c \times \exp\left(\frac{A}{Temperature}\right)$$

With N<sub>2</sub>O in mg/Nm<sup>3</sup>, dry and at 6vol.% O<sub>2</sub>. With a, b, c and A as constants. C3 is a constant as well, with a dimension of Nm<sup>3</sup>/GJ. Curve fitting resulted in: A = 8100, with as unity K, a = 0.8, b = 1, c = 4.4, and C3 = 1.31 x 10<sup>-4</sup>, using data from (VGB, 1992, 14 V-27). This gives following correlation:

$$N_2O = 1.31 \times 10^{-4} \times FR^{0.8} \times N^1 \times \Lambda^{4.4} \times \exp\left(\frac{8100}{Temperature}\right) \quad (6)$$

Depending on the set of data used, other values could be assumed, such as: A = 15 000 (K), c = 4 to 6, a = 0.5 to 0.8, b = 1, C3 = 1.17 x 10<sup>-7</sup> (Nm<sup>3</sup>/GJ) (VGB, 1992, 14, V-27); and A = 17 500 (K), c = 0, a = 0.6, b = 1, C3 = 3.02 x 10<sup>-8</sup> (Nm<sup>3</sup>/GJ) (VGB, 1992, 14 V-28). According to Cai (2015), the value of c can be 0, positive or negative, depending on the literature cited. According to (Basu, 2006; VGB, 1992, 14 V-28), the value of c is almost 0, or slightly positive.

Other correlations for N<sub>2</sub>O are proposed as well (van Dijken, 2013). According to the models presented here, the primary N<sub>2</sub>O is very low with firing wood, as both FR and the specific N-content are very low. Also according to this model, the primary N<sub>2</sub>O is low with firing lignite, as the FR is low.

Table 6 presents the values of C3, as calculated with equation 6, for b = 1. Which value of b is correct?

The factor C3 seems hardly dependent on the unit (VGB, 1992, 14 V-28). In contrast, table 6 strongly suggests that the value of C3 depends on the unit. The factor C3 varies with a factor of about 5, depending on the unit! Possibly also this difference is related to:

- A different ratio of primary to secondary air
- The height of the secondary air ports above the bottom
- The cyclone separation efficiency
- Flue gas residence time
- “Limestone addition”
- Etcetera.

Table 6: Calculated values for C3, with  $b = 1$  (= N1).

Unit	Test	C3
Polaniec	Wet wood chips + 20wt.% PKS	$0.32 \times 10^{-4}$
Pforzheim	Coal 1	$1.4 \times 10^{-4}$
	Coal 2	$0.94 \times 10^{-4}$
	Coal 4	$1.4 \times 10^{-4}$
Saarbrücken	Coal 3	$0.73 \times 10^{-4}$
	Coal 4	$0.85 \times 10^{-4}$
Cologne	Lignite 1	$0.26 \times 10^{-4}$
Orebro	Coal 1	$0.40 \times 10^{-4}$
	Coal 2	$0.37 \times 10^{-4}$
	Wood chips	$0.36 \times 10^{-4}$

## DESIGN

The design of the CFBC has a significant influence on the primary emissions of  $N_2O$  and  $NO_x$ . Design here means aspects such as:

- Cyclones separation efficiency
- Air staging, like ratio of primary to secondary air, height of the secondary air ports above the bottom
- Residence time of the flue gas
- Post combustion
- “Limestone addition”
- Bed material, like fineness, composition, quantity, catalytic activity
- Flue gas recirculation.

Such design aspects (easily) explain for the variations in the values of C2 and C3 as observed. Especially a high cyclones separation efficiency and air staging with sufficient height of the secondary air ports contribute to low primary emissions of  $NO_x$  (and  $N_2O$ ) (Yu Jen Sung, 1995; Zhao, 1992; Stamatelopoulos, 2008; Kobylecki, 2008).

Table 7 presents the effect of important design parameters, according to literature. It is important to note that the amount of limestone added to the bed is very important. The values presented in table 7 are for molar ratio's of Ca to S of about 3. When less limestone is added, the effect is reduced. Amand (1992) mentions higher factors with bituminous coal-firing, of about 6 with a Ca to S molar ratio of about 4.3, and of about 4

with a Ca to S molar ratio of about 2.1. Bituminous coal with about 2.7 wt.% S, dry and ash free, was fired (Amand, 1992).

Table 7: The influence of important CFBC design parameters on primary N<sub>2</sub>O and NO<sub>x</sub>, as multiplication factor.

Parameter	NO <sub>x</sub>	N <sub>2</sub> O	References NO <sub>x</sub> , N <sub>2</sub> O
High separation efficiency cyclone	0.5 to 0.67, decrease	Up to 1.4, increase	(Kobylecki, 2008; Bramer, 1991), (Oka, 2004; Bramer, 1991)
Height of secondary air ports above bottom	0.85, decrease	0.85, decrease	(Zhao, 1992), (Yu Jen Sung, 1995)
Limestone addition	1.5 to 2.0 (and more), increase, with coal  Down to 0.25, decrease, with pet cokes 1.05, increase, with pitch	Down to 0.75, decrease, with coal  Down to 0.75, decrease, with pet cokes Down to 0.7, decrease, with pitch	(VGB, 1994; Zhao, 1992; Amand, 1992), (VGB, 1994; Yu Jen Sung, 1995) (Zhao, 1992), (Yu Jen Sung, 1995) (Yu Jen Sung, 1995; Zhao, 1992), (Yu Jen Sung, 1995)
	8 (and more), in total: from 0.25 to 2.0.	2 (and more) in total, from 0.7 to 1.4	

Whether the primary NO<sub>x</sub> emissions increase or decrease upon “limestone addition”, and by which multiplication factor, seems to depend on the ratio char-N to total-N of the fuel, or in other words on the ratio of N-FC to N-VM of the fuel (Yu Jen Sung, 1995).

A high cyclone separation efficiency increases the content of UBC in the bed. As can be anticipated from eq. (5), this results in reduced emissions of NO<sub>x</sub>, which is confirmed by literature regarding measurements (Kobylecki, 2008). No literature regarding measurements of the influence of high cyclone separation efficiency on primary N<sub>2</sub>O emissions was found. However, (Oka, 2004; Bramer, 1991) suggest an increase of N<sub>2</sub>O emissions with increasing fly ash recirculation. When this is due to increase of UBC of the bed, it is in agreement with eq. (6), when assuming a direct relation between UBC and FR. Boerrigter (2004) suggests that the N-FC can also directly and indirectly form N<sub>2</sub>O. So, when UBC is high, FR is high, N-FC is usually high as well, and formation of N<sub>2</sub>O is high as well.

With table 7, it is assumed that the effects are cumulative. With table 7, only 2 references were found regarding the effect of the high separation efficiency cyclone on N<sub>2</sub>O emissions. With these references, tests were performed using a small-scale fluidized bed.

The author in general advocates not to add limestone to the bed, but application of the semi wet/dry FGD, like spray drying absorption using an aqueous Ca(OH)<sub>2</sub> suspension, or preferably the wet limestone-gypsum process, see also van Dijen (2010) and Minhua (?).

When limestone is added to the bed, operating at temperatures of more than 800°C, the bed does finally not contain limestone, but compounds such as CaO, CaSO<sub>4</sub>, etcetera. According to the literature, these compounds act as catalyst regarding formation and reduction of NO<sub>x</sub> and N<sub>2</sub>O. This catalytic activity depends on:

- The quantity of limestone added
- The fuel
- Possibly, the quality of the limestone (Zhao, 1992).

## CONCLUSIONS

Mathematical models / equations are presented regarding primary NO<sub>x</sub> of PFC and CFBC. A mathematical model / equation is also presented regarding primary N<sub>2</sub>O of CFBC. The models for CFBC do not hold for co-combustion and can be applied with the fuels hard-coal, lignite and wood. The models possibly hold for the fuel pet cokes as well, but the data available for this paper is (too) limited.

The accuracy of the CFBC models regarding primary NO<sub>x</sub> and primary N<sub>2</sub>O is limited. For instance, aspects like air staging, catalytic activity of the ash and bed material, bed inventory, cyclone separation efficiency, limestone addition, flue gas residence time, etcetera, are not (yet) modelled. However, they can be applied for qualitative predictions, for instance with a change of fuel or with changing operating parameters.

The design of the CFBC has a significant influence on primary emissions of N<sub>2</sub>O and NO<sub>x</sub>. Attention is paid to the CFBC design parameters and their influence on primary emissions of NO<sub>x</sub> and N<sub>2</sub>O, especially high efficiency cyclones, "limestone addition" and the height of secondary air ports above the bottom. These design parameters easily explain for the variations of primary NO<sub>x</sub> and primary N<sub>2</sub>O emissions encountered and modelled.

The presence of catalytically active elements, like Na, K, Fe, Mg and Ca, in the fuel, the ash and the bed material must be considered as well, which is often not the case in literature. For instance wood is usually rich in K and Ca, and lignite can be rich in Ca. This also means: where there are rules, there are exceptions as well.

The addition of limestone to the bed can increase primary NO<sub>x</sub> drastically, depending on the fuel, and hence in such cases limestone addition is definitely a bad idea.

There is room for further research regarding this subject of modelling of primary NO<sub>x</sub> and N<sub>2</sub>O, especially regarding CFBC, like:

- Is there thermal NO<sub>x</sub> with CFBC?
- Co-combustion
- Other fuels, like dry municipal sewage sludge and pet cokes
- CFD modelling of CFBC regarding primary NO<sub>x</sub>, primary N<sub>2</sub>O and SNCR
- The effect of increasing Lambda on primary N<sub>2</sub>O and its cause.

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