Minnkota Power
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Nov 17, 2008

Received
Air Quality
NOV 2008

Mr. Terry O'Clair
Director, Division of Air Quality
North Dakota Department of Health
918 E. Divide Avenue, 2nd Fl
Bismarck, ND 58501-1947

Re: Response to EPA's October 17, 2008 Response to Minnkota's Letter on Public Comments Received on the North Dakota Department of Health's Preliminary NOx BACT Determination for M.R. Young Station

Dear Mr. O'Clair:

Enclosed, please find Minnkota's response to EPA's October 17, 2008 comments. In addition to the response enclosed, Minnkota also makes the following comments.

The North Dakota Department of Public Health ("NDDH") has led an intensive, two-year process designed to determine what constitutes Best Available Control Technology ("BACT") at Minnkota's Young Station. NDDH has collected an administrative record that spans over a thousand pages of highly detailed, deeply technical engineering analyses. NDDH has also managed a highly-transparent, public decision-making process that has solicited the input of EPA at numerous times during the administrative decision-making process, and has also solicited public comment. NDDH itself has engaged in a vigorous and challenging exchange with Minnkota over engineering reports and analyses. We believe NDDH has more than satisfied its responsibilities under the July 2006 consent decree and its own regulatory BACT requirements.

We find the October 2008, comments of EPA's "expert witness" to be mostly redundant of earlier comments by EPA that NDDH fairly addressed previously. We do not believe EPA's October 17, 2008, comments warrant any modification to NDDH's BACT Determination.

We have set forth in the following sections in more detail the grounds in support of our response.

NDDH's Decision is Reasonable (Not Arbitrary nor Capricious), Supported by the Record, and Entitled to Substantial Deference

From EPA's comments, it is evident that there exists a difference in opinion regarding what constitutes BACT at Young Station: NDDH has concluded that SCR is technically infeasible; EPA insists that it is technically feasible. In such disputes, the North Dakota Supreme Court's opinion in *People to Save the Sheyenne River, Inc. v. North Dakota Dept. of Health*, 697 N.W.2d 319 (N.D. 2005) describes the standard of review applied to challenges of NDDH permitting decisions.

In that case, the plaintiffs—including the government of the Province of Manitoba—challenged a North Dakota Pollutant Discharge Elimination System ("NDPDES") permit that NDDH issued under the Clean Water Act.[1] Plaintiffs disputed NDDH's findings and decisions on technical matters ranging from phosphorus loading, to anti-degradation of water quality, to the presence and potential impacts of the parasites *gyrodactylus hoffmani* and *ligula intestinalis*. The court held that NDDH's permitting decision would be set aside only if it was "arbitrary, capricious, or unreasonable." *Id.* at 329. *See also People to Save the Sheyenne River, Inc. v. North Dakota Dept. of Health*, 744 N.W.2d 748, 753 (N.D. 2008) (applying arbitrary, capricious, and unreasonable standard to NDDH modification of NDPDES permit). The court more fully described the standard of review as follows: "A decision is arbitrary, capricious, or unreasonable if it is not the product of a rational mental process by which the facts and the law relied upon are considered together for the purpose of achieving a reasoned and reasonable interpretation." *People to Save the Sheyenne River*, 697 N.W.2d at 329; *see also Little v. Traynor*, 565 N.W.2d 766, 773 (N.D. 1997). And an administrative record is "adequate if it enables [a reviewing court] to discern the rationale for the decision." *Id.* Moreover, the North Dakota Supreme Court has held "[t]hat deferential standard is particularly applicable where, as here, the subject matter is complex or technical and involves agency expertise." *People to Save the Sheyenne River*, 697 N.W.2d at 329. The court upheld NDDH's permitting decision on every ground, finding sufficient evidence in the record to support NDDH's determinations, and holding that the determinations were not arbitrary, capricious, or unreasonable. *Id.* at 333.

Here too, NDDH's BACT Determination is entitled to substantial deference, and may only be overturned—regardless of EPA or others' comments—if NDDH's decision was arbitrary, capricious, or unreasonable.[2] That is, NDDH's decision may only be set aside if—based on the record before it—NDDH's decision was the product of an irrational mental process or if the court can discern no rationale for the decision. Under this deferential standard of review, it is relatively unimportant that EPA may very well have interpreted the Coyote Station pilot project results differently, or have a different interpretation of the impact of fuel variability on control performance, or have a different view on whether or not a TESCR will work, or a different view on any of a dozen other issues. The question is whether NDDH engaged in a rational mental process based on evidence in the record. And here, the record is replete with extremely detailed technical materials that are sufficient to support

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[1] NDDH has delegated authority to implement the federal NPDES program, much like NDDH also as SIP-approved authority to implement the federal PSD program. The use of the arbitrary and capricious standard of review is accordingly equally as applicable to NDDH's PSD program as it was to its NDPDES program.

[2] The Consent Decree standard of review is not inconsistent with the North Dakota requirement that administrative decisions not be unreasonable and that they must find support in the administrative record. *See* Consent Decree ¶ 147(c) ("The Court shall sustain the decision by NDDH unless the Party disputing the BACT Determination demonstrates that it is not supported by the state administrative record and not reasonable in light of applicable statutory and regulatory provisions.").

NDDH's conclusions, EPA's own views to the contrary notwithstanding. For example, NDDH challenged Minnkota's initial submissions relating to the BACT Determination, and certainly considered EPA comments on interim drafts, as well as the opinions of those other than Minnkota. These factors are quite useful in determining that an agency acted reasonably in making a decision based on the record before it. *See, e.g.*, *Citizens for Clean Air & Water in Pueblo and Southern Colorado v. Colorado Dep't of Public Health and Envt.*, 181 P.3d 393, 398 (Col. App. 2008), *cert. denied*, 2008 WL 2581591 (Colo. June 30, 2008) (citing as evidence of rational decision-making a state's challenge and disagreement with a source's BACT input, as well as its examination of other sources of information). The extensive record here—and NDDH's careful treatment of it—is evidence that NDDH engaged in a rational mental process in reaching its BACT Determination.

Furthermore, EPA bears the burden of proof that NDDH acted arbitrarily, capriciously, or unreasonably. The Consent Decree expressly provides that "The Court *shall sustain* the decision by NDDH *unless* the Party disputing the BACT Determination demonstrates that it is not supported . . . ." *See* Consent Decree ¶ 147(c) (emphases added). EPA carries a very heavy burden in seeking to overturn NDDH's reasonable BACT Determination.

Technical Disagreements do not Render NDDH's Decision Arbitrary, Capricious, or Unreasonable

With the proper legal standard firmly in mind, it is clear that none of the comments by EPA or the DOJ's consultant prove that NDDH has acted arbitrarily, capriciously, or unreasonably. Mere disagreement regarding the interpretation of data, or alternative exercises of engineering judgment simply do not disqualify NDDH's BACT Determination.

In summary, with the additional of the enclosed response to EPA's October 17, 2008 comments, the administrative record is replete with sophisticated engineering and technical information upon which NDDH can make a defensible and rational BACT Determination. While EPA may disagree with NDDH's decision, mere disagreement is no ground for disturbing its decision. We urge NDDH to finalize its BACT Determination as currently drafted so that Minnkota get on with the work of installing BACT controls to reduce nitrogen oxides emissions at Milton R. Young Station.

Should you have any questions concerning the above or the enclosed, please contact me at 701-795-4221.

Yours truly,

MINNKOTA POWER COOPERATIVE, INC.

John T. Graves

John T. Graves, P.E.
Environmental Manager

C: David Sogard
Luther Kvernen
Plant file

Responses to Hans Hartenstein's October 2008 Remarks to September 22, 2008 Comments & Responses on NDDH Preliminary NOx BACT Determination for Milton R. Young Station (MRYS)

November 17, 2008

Burns & McDonnell (B&McD), and its SCR consultant, Fuel Tech[1], along with Steve Benson of the Department of Chemical Engineering at the University of North Dakota[2], have reviewed the October 2008 remarks of the United States' Department of Justice's (DOJ's) commenter, Hans Hartenstein (Hartenstein, 2008), provided by the United States Environmental Protection Agency (U.S. EPA or EPA) Region 8 Office of Enforcement, Compliance, and Environmental Justice and forwarded by the North Dakota Department of Health (NDDH). These are responses regarding selective catalytic reduction (SCR) technology feasibility pertaining to the NDDH's Preliminary NO_X BACT Determination for Nitrogen Oxides for Milton R. Young Station Units 1 and 2, dated June 2008 (NDDH, 2008).

We continue to believe that the administrative record fully supports a finding by the NDDH that separated over-fire air (SOFA) in conjunction with selective non-catalytic reduction (SNCR) technology is Best Available Control Technology for electric generating units that utilize cyclone burners firing North Dakota lignite. The following sections address specific topics mentioned in the EPA's comments and other issues in greater detail.

- Mass Particulate Loading Irrelevant to SCR Catalyst Deactivation from Aerosol Poisons
- Biomass Firing Impacts on SCR Catalyst as Surrogate for North Dakota Lignite
- General Regulatory Considerations
- Corrections, Clarification and Omissions of Hartenstein's Remarks
  - Responses to General Remarks
  - Responses to Specific Comments
- Conclusions

[1] formerly Tackticks LLC.
[2] formerly employed by Energy & Environmental Research Center (EERC) of the University of North Dakota.

Mass Particulate Loading Irrelevant to SCR Catalyst Deactivation from Aerosol Poisons

As previously described in the September 22, 2008 comments and responses (Burns & McDonnell and others, September 2008), the catalyst in any configuration of SCR application for a high-sodium North Dakota lignite-fired cyclone boiler is expected to be exposed to appreciable concentrations of sodium, potassium, and other alkali-rich aerosols. These constituents are released from the combustion cyclones and are not effectively removed from the flue gas streams by the electrostatic precipitator and flue gas desulfurization systems ("scrubbers"). Air quality control equipment vendors have historically not guaranteed removal rates of such particles and aerosols. These materials react with other gas phase species and deposited particles that will cause blinding or can react with active sites in the catalyst pores, causing poisoning and deactivation, thus rendering the NOx reduction capability ineffective.

Lignite coals contain high levels elements such as sodium, magnesium, and calcium that are associated with the organic or combustible fraction of the coal. These elements are prone to form gas phase species and very small particles during combustion and gas-cooling processes. Specifically, sodium will vaporize during coal combustion and condense in the convective pass of the boiler upon gas cooling. Sodium will condense heterogeneously on the surfaces of other fly ash particles or homogeneously to aerosols. In addition, the high temperature cyclone-firing of these coals increase the level of aerosols downstream in the combustion system. This is because the high operating temperature increases vaporization and also some of the ash available for heterogeneous condensation downstream is removed as slag. The resulting aerosol produced upon gas cooling is enriched in sodium and potassium. These sodium and potassium-rich aerosols are very reactive with gas phase constituents and other materials with which they come into contact. The form of sodium in the submicron particulate phase is as oxides, hydroxides, and sulfate. In addition, the abundance of the submicron fraction is dependent upon the ash content of the coals. Typically, coals that contain high levels of organically associated elements and lower levels of ash—typically less than 15% (dry basis)—have the potential to produce high levels of the submicron, homogeneously condensed sodium and potassium-rich aerosol.

As indicated by EPA (Woodward, 1998), scrubbers do not effectively remove particulate less than 1 μm in diameter. There is significant evidence that sodium-rich aerosols penetrate ESPs as well as scrubbers at full-scale power plants when firing high-alkali-containing fuels. An example is a biomass fired system using a tower type scrubber where the removal efficiency of the smaller size fraction of ash is low, as shown in Figure 1 (Ohlström and others, 2006).

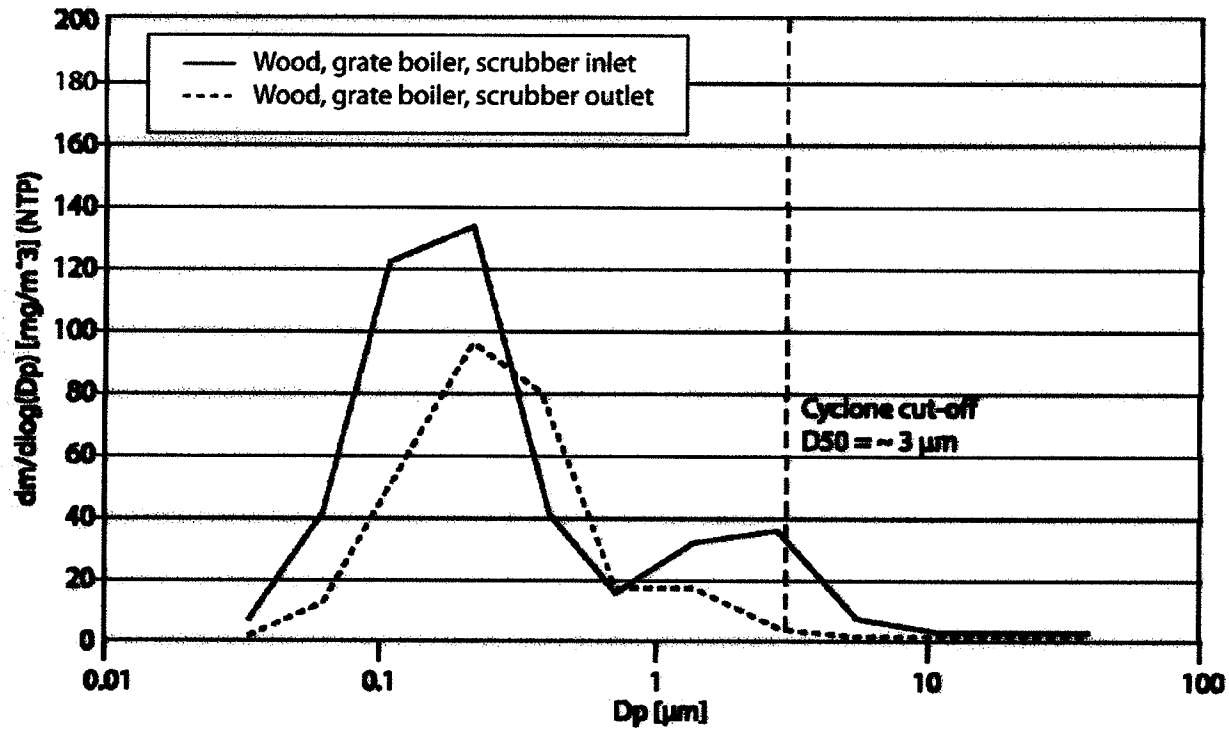

Figure 1. Removal of fine aerosols using a scrubber on a wood fired combustor (Ohlström and others, 2006).

Minnesota Power's Boswell Energy Station found that when it fired high-sodium, lower-ash northern Powder River Basin subbituminous coal (7% Na_2O in the ash), it experienced increases in opacity. Hurley and Katrinak (1992) conducted a field-testing project on Unit No. 4, a pulverized coal-fired boiler equipped with a venturi wet scrubber, to better understand the reasons for the opacity problems. During the field testing, sampling of the coals, flue gases, and scrubber materials was conducted. The particulate in flue gases downstream of the scrubber was aerodynamically classified using a multicyclone followed by an impactor and a Nucleopore filter. The sized fractions were weighed and analyzed to determine the abundance and composition of the submicron-sized fractions. The mass loadings in the various size bins are

plotted in Figure 2, showing that the scrubber is quite effective in removing the larger particles. However, the scrubber is not very effective in removing the aerosols less than 1 micrometer in diameter for both the blended coal and the high sodium coal (Coal A).

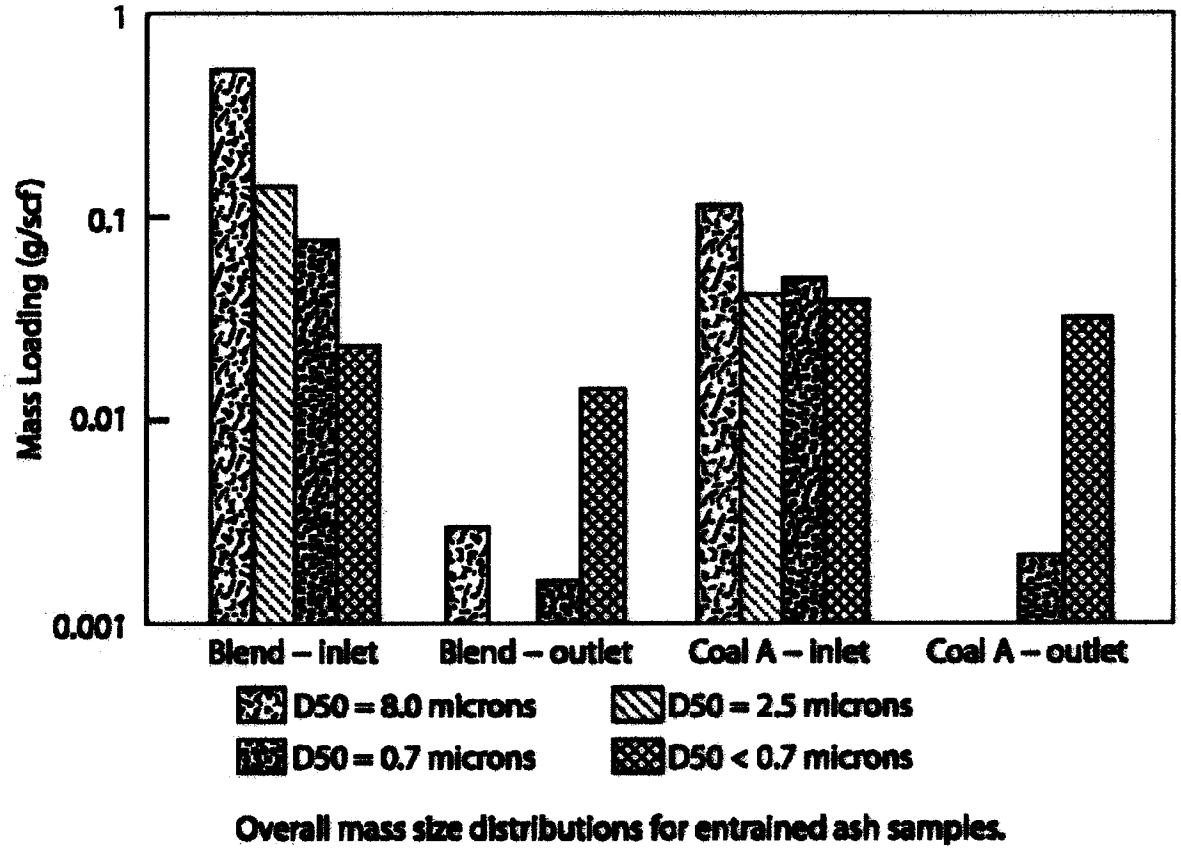

Figure 2. Mass loadings and size for particulate collected upstream and downstream of the wet venturi scrubber at Clay Boswell (Hurley and Katrinak, 1992).

The results of the study indicated that the particulate collected downstream of the scrubber was coal-related and caused by the high sodium content of the coals. Vapor-phase sodium condenses in the boiler's convective pass to form fine sodium-rich aerosols or other Na species that later react with ash particles. Pure Na_2SO_4 particles are too small to be removed by such scrubbing, despite the fact that they are highly soluble in water. Figure 3 shows the spikes of the ash material collected on Stage 10 of the impactor. This impactor accumulation represents the 0.7 to 2.5 micrometer size fraction of the aerosol. The spikes are made up of fine particulate matter, and the chemical analyses of the spikes and ash particles collected on the Nucleopore filters downstream of the impactor plates represent the <0.7 micrometer aerosols are shown in Table 1.

Both samples are dominated by sodium and sulfur that are likely in the form of sodium sulfate. These sulfate materials exhibit highly cohesive tendencies.

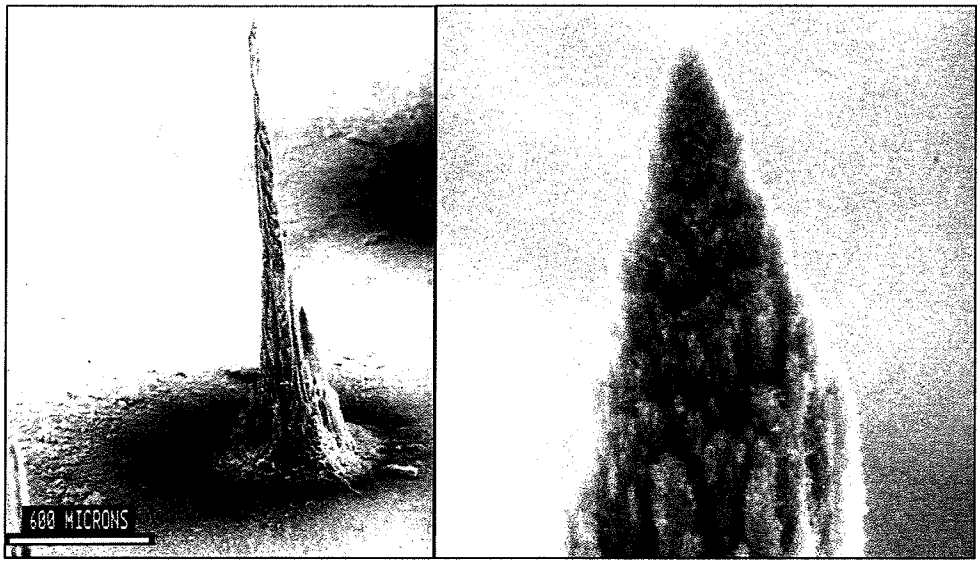

Figure 3. Scanning electron microscope images of spikes formed on impactor plates when high-sodium subbituminous coal is combusted (the picture on the right is a close-up of the spike) (Hurley and Katrinak, 1992).

Table 1. Chemical Composition of the Spike Shown in Figure 3 and the Nucleopore Filter (weight percent expressed as equivalent oxide).

	100% Coal A	
Oxide	**Spike**	**Filter**
Na_2O	**35.1**	17.3
MgO	1.4	7.8
Al_2O_3	2.0	9.8
SiO_2	9.1	10.6
P_2O_5	0.4	0.2
SO_3	**39.7**	28.0
K_2O	2.6	1.5
CaO	6.2	15.7
TiO_2	0.2	1.8
Cr_2O_3	1.4	0.1
Fe_2O_3	0.9	2.9
BaO	0.5	2.6

The ash particles collected on the Nucleopore filters downstream of the impactor were further characterized on a particle-by-particle basis with a scanning electron microscopy and x-ray

microanalysis (Hurley and Katrinak, 1992). The chemical analysis of particles collected on the filter downstream of the scrubber when firing 100% Coal A (high sodium coal) are shown in Table 2. The individual particles have sodium levels as high as 63%. The particles with 0 diameter were particles where the exact diameter could not be determined because of particle agglomeration.

Table 2. Elemental compositions of mixed submicron particles collected during the combustion of Coal A (high sodium subbituminous coal) at the scrubber outlet. Particles sorted by diameter in micrometers. The chemical composition is reported as elemental weight percent (Hurley and Katrinak, 1992).

Ptcl	#	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Ba	Ti	Diameter
1		16	35	3	29	0	0	0	0	3	3	0	12	0
2		41	24	0	0	14	0	0	10	0	0	1	10	0
3		0	32	0	28	0	10	0	4	22	4	0	0	0.1
4		0	17	43	0	2	0	5	18	5	2	8	0	0.1
5		0	21	0	26	15	0	7	21	0	3	7	0	0.3
6		28	28	0	26	0	0	0	1	14	0	3	0	0.3
7		57	0	0	11	0	0	6	12	0	0	0	14	0.3
8		24	0	0	24	0	8	0	11	20	2	0	11	0.3
9		16	14	12	31	10	3	3	0	1	2	8	0	0.3
10		0	18	2	27	6	9	0	11	21	2	4	0	0.4
11		23	0	12	25	6	0	0	9	12	2	6	5	0.4
12		44	17	0	0	9	9	4	0	5	1	6	5	0.5
13		63	19	0	14	3	0	0	0	0	0	1	0	0.5
14		9	30	0	9	4	9	0	6	13	2	8	9	0.5
15		25	9	1	26	12	5	0	0	11	2	2	8	0.5
16		38	0	0	38	0	12	1	2	1	3	0	5	0.5
17		50	0	32	9	4	0	0	0	0	3	0	4	0.6
18		20	0	26	15	0	12	10	9	0	3	5	0	0.6
19		21	0	33	31	0	0	0	9	3	2	0	0	0.6
20		28	0	13	13	11	12	0	5	5	2	5	5	0.6
21		38	0	10	10	11	14	0	7	6	0	3	2	0.7
22		21	5	13	21	10	8	8	0	9	0	3	3	0.7
23		31	6	14	21	7	3	0	3	6	1	4	4	0.7
24		51	0	2	15	10	10	5	1	0	1	0	7	0.7
25		29	3	17	21	15	11	0	0	0	0	3	3	0.7
26		42	21	0	0	0	12	7	0	9	3	0	5	0.7
27		37	0	38	0	4	3	0	0	13	0	7	0	0.8
28		40	0	0	23	0	6	13	5	0	2	6	5	0.8
29		42	13	0	33	0	6	0	0	6	2	0	0	0.8
30		49	0	0	8	1	11	8	7	3	2	5	4	0.8
31		47	8	14	8	9	7	0	3	0	1	4	0	0.9
32		43	0	4	10	13	15	8	4	0	1	0	2	0.9

Fly ash produced upon the combustion of high sodium lignites in a pulverized coal (PC) fired system shows significant enrichment of sodium in the smaller size fractions as shown in Figure 4. This figure illustrates the increase in the sodium content in the finer size fractions of ash as a result of firing high sodium lignite. The sodium and sulfur content of the less that 3 micrometer

size fraction of the sampling train approached 20% Na_2O, and 25% SO_3. The form of the sodium is likely sodium sulfate.

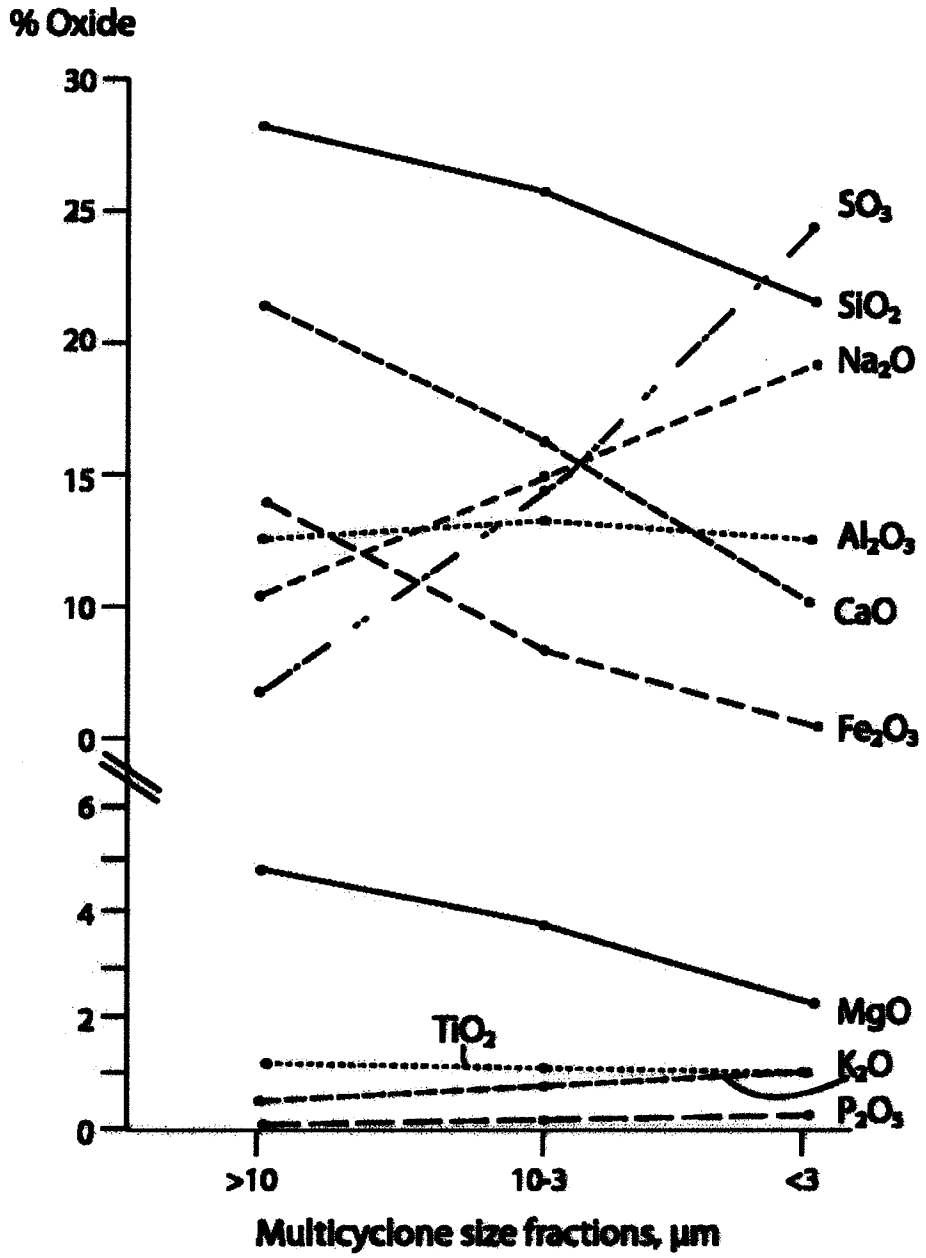

Figure 4. Composition distribution of ash particles during combustion of North Dakota Lignite (Benson and others, 1984).

The abundance of sulfate aerosols was measured at the MRY by Markowski and others, 1983. The results of the measurements of aerosol capture are illustrated in Figure 5. The results show

that aerosols less than one micrometer in diameter are not effectively captured in the ESP and wet FGD at the MRY facility. The graph also indicates the penetration of the particles through the FGD as a function of particle size. The penetration is the outlet size distribution divided by the inlet size distribution. (Penetration = 1- efficiency). The results showed that the "metallic" sulfate aerosols (sodium sulfate) penetrated the FGD much more effectively than the larger particulate.

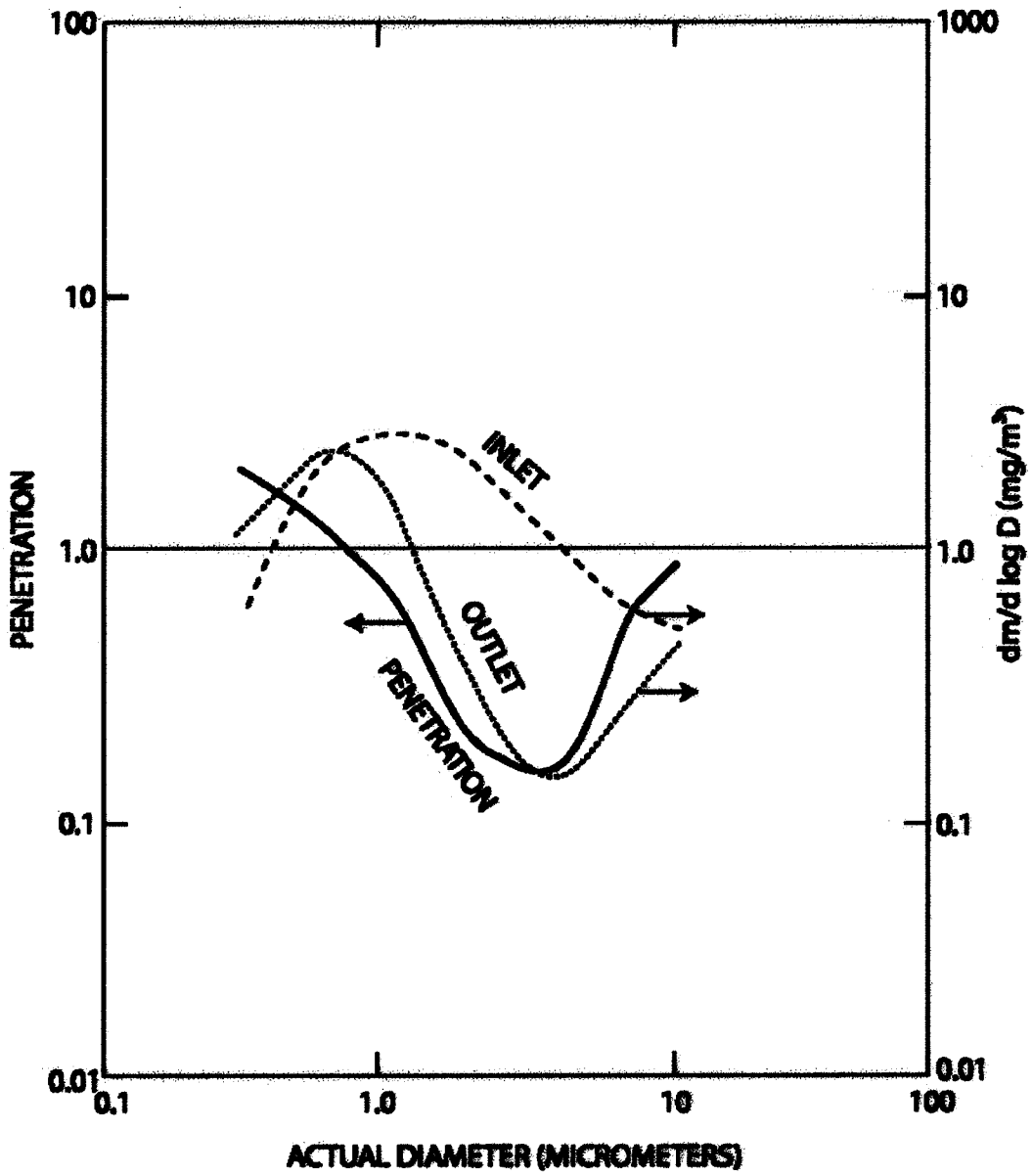

Figure 5. Penetration of aerosols through the MRY Unit 2 wet scrubber (Markowski and others, 1983).

Sodium and potassium rich aerosols are present in the flue gases entering the FGD as evidenced by the recent work conducted by Tolbert and others (2008). Testing of Power Span's barrier discharge reactor being developed for new power generation was conducted to determine the impact of sodium rich aerosols on the performance of the PowerSpan ECO Technology for flue gases from boilers firing high sodium ND lignite. The barrier discharge reactor is placed downstream of particulate control systems to enable the oxidation of NO to NO_3 species that will allow for capture in an ammonia based scrubbing system. A slip stream barrier discharge reactor system was designed by PowerSpan and the EERC and installed downstream of the ESP on Unit 1 at the MRY station. The gas temperature entering the barrier reactor was approximately 300 °F. The primary concern regarding the success of the technology was that sodium-rich aerosols present in the flue gas stream would diffuse to the surface of the quartz rod and become bonded to it, resulting in decreased performance of the barrier discharge reactor. The ash accumulation resulted in decreased NO oxidation due to accumulations of alkali and alkaline earth sulfate rich ash layer on the rods. The bulk composition of ash scraped from selected quartz rods was determined by x-ray fluorescence (XRF). The rods sampled were from three electrodes that were sampled at 20, 48, and 107 days. The bulk composition summarized in Table 3 shows significant levels of sodium, calcium, and potassium along with sulfur.

Table 3. Bulk composition of ash removed from electrode samples obtained from rod removed at 20, 48, and 107 days.

Oxides (wt.%)	(a)	(b)	(c)	Elemental (wt.%)	(d)	(e)
SiO_2	10.3	10.8	22.0	Si	9.6	15.8
Al_2O_3	4.1	4.3	8.8	Al	4.4	7.2
Fe_2O_3	4.3	4.5	9.2	Fe	6.0	9.8
TiO_2	0.2	0.2	0.4	Ti	0.2	0.4
P_2O_5	0.1	0.1	0.2	P	0.1	0.2
CaO	10.5	11.0	22.5	Ca	15.1	24.7
MgO	2.1	2.2	4.4	Mg	2.5	4.1
Na_2O	11.7	12.3	25.1	Na	17.4	28.5
K_2O	3.4	3.6	7.3	K	5.7	9.3
SO_3	48.5	51.0	-----	S	39.0	-----
Total	95.0					

(a) Oxide concentrations (wt.%) on an ash basis.
(b) Oxide concentrations normalized to a closure of 100%.
(c) Oxide concentrations renormalized to a SO3-free basis.
(d) Elemental concentrations (wt.%) on an ash basis.
(e) Elemental concentrations renormalized to a S-free basis.

Comments: BaO = 0.87% Unknowns = 3.54%
SrO = 0.34%

Biomass Firing Impacts on SCR Catalyst as Surrogate for North Dakota Lignite

North Dakota lignite and biomass materials have similar associations of alkali elements. The bonding sites for alkali elements such as sodium and potassium in biomass and lignite coals are organic acid sites. The alkali elements are present in coal and biomass as salts of organic acid groups, such as carboxylic acids. The associations of alkali and alkaline earth elements have been extensively studied by the EERC (Benson and Holm, 1983 and Benson and others, 1994). The alkali elements associated with biomass have been extensively studied by Sandia National Laboratory (Miles and others, 1995). Both studies conclude that alkali and alkaline earth elements are bonded to the organic matrix of the lignite or biomass. In addition, the behavior during combustion and gas cooling is similar. Organically associated alkali elements will

vaporize during the combustion process and produce highly reactive vapors and aerosols (Benson and other, 1984 and Ohlström and others, 2006).

Khodayari (2001) exposed catalysts to flue gases in a PC unit firing a low ash wood and in a CFB unit firing high ash forest residues and measured relative reactivity as illustrated in Figure 6.

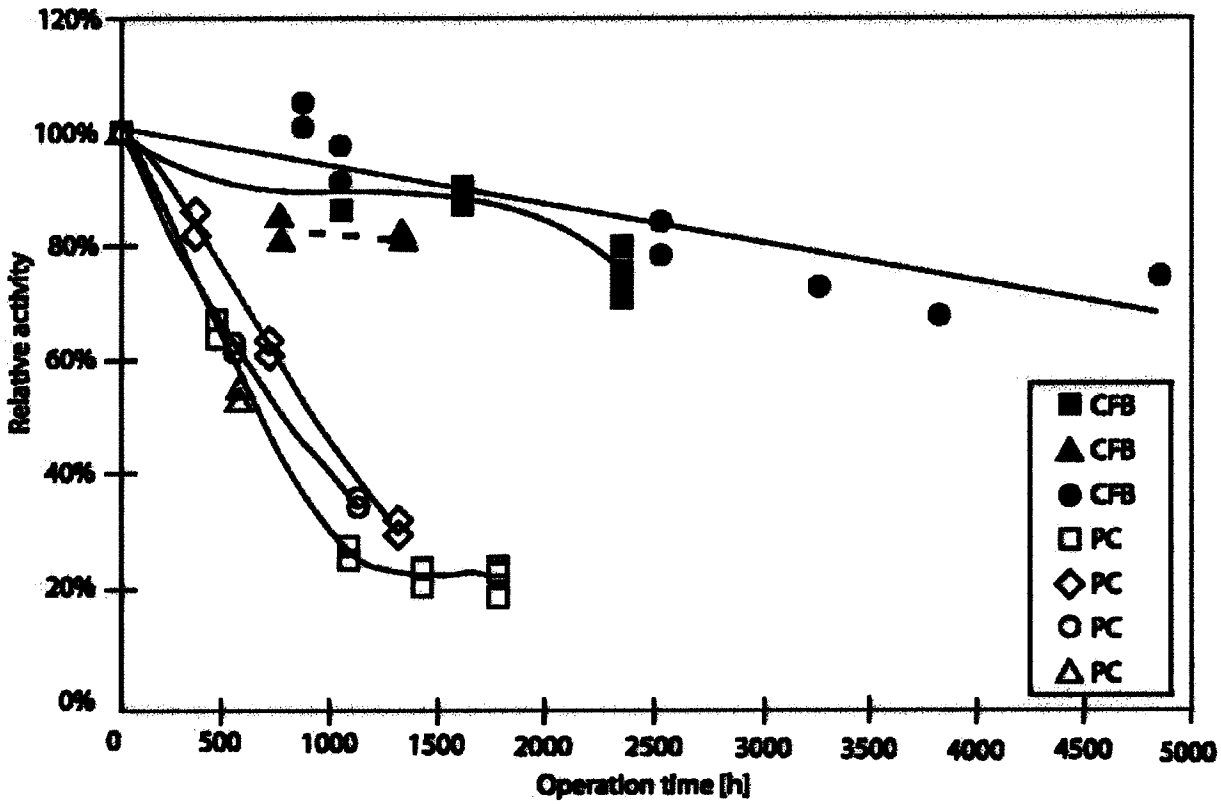

Figure 6. Comparison of poisoning of catalysts in a CFB boiler firing forest residues, and in a PC firing pulverized wood (Khodayari, 2001).

Khodayari found that the degree of deactivation was related to the abundance of potassium and sodium that accumulated in the catalyst and not related to ash loading. In the CFB boiler exposed catalyst, the level of potassium accumulated in the catalyst was 0.27% and the relative reactivity of the catalyst decreased to about 78%, or 22% deactivation. For the PC case in firing wood, the build up of potassium in the catalyst was 0.8 % after 1400 hours and the relative reactivity decreased to 20%, or 80% deactivation. The higher deactivation exhibited for the PC case firing wood was due to the presence of highly reactive alkali (potassium and sodium) aerosols in the flue gas. The PC system produced more highly-reactive alkali aerosols because

of higher firing temperatures causing an increase in the vaporization of alkali and low ash content of the wood that reduces the sites for condensation of alkali vapors. Lower levels of highly-reactive alkali aerosols are produced in the CFB case because of the lower operating temperatures, higher ash content of the forest residue, and higher particle loading in a CFB as compared to the PC system. The alkali in the CFB system reacts with bed materials and ash particles during circulation decreasing the abundance of alkali aerosols. The reactive alkali aerosols diffuse into the catalyst and are adsorbed chemically and physically on the catalyst surfaces resulting in deactivation. Higher temperatures such as those found in cyclone fired system will cause an increase in vaporization of alkali species and exacerbating the formation of reactive alkali aerosols.

Numerous investigations have shown that alkali (sodium and potassium) rich aerosols degrade catalyst performance as follows:

- Zheng and others (2005) biomass derived alkali rich aerosols caused a drop in NOx reduction activity by 52% after about 1140 hours of operation.
- Chen and others (1990) examined the poisoning mechanisms of alkali and alkaline earth oxides on vanadia catalysts and found that the deactivation is directly related to the basicity of the poisons and found a decrease in NO reduction rate constant from 10 to 2.5 cm^3/g s for sodium oxide.
- Guo (2006) conducted a study of the intrinsic SCR activity for NO with NH_3 reaction and found that the additions of K, Na, and Ca greatly decrease the NO reduction activity of 1% V_2O_5 – 9% WO_3/TiO_2. A decrease in NO reduction rate constant from 18 to 5 cm^3/g s for potassium oxide was measured.
- Kling and others (2007) investigated deactivation of SCR catalysts in three biomass and peat fired 100 MW-scale combustion systems. They found that the increased levels of sodium and potassium accumulated in the SCR catalyst was derived from the ultra fine particles (aerosols). These accumulations of aerosols decreased the NOx reduction catalytic activity by over 40% in testing ranging from 100 to 3000 hours.
- Strege and others (2008) at a stoker-fired utility boiler firing a blend of biomass and Powder River Basin coal (PRB) found that the catalyst deactivation rate was about 18% per 1000 hours.

- Khodayari and others (2000) lost 80% of reactivity after being exposed to flue gas derived from firing wood for about 1400 hours.
- Zhang and others (2008) investigated the operation of full-length monolith catalysts installed at a straw-fired power plant and found a high deactivation rate of about 1% of the relative activity per day was observed when the power plant ran continuously.

General Regulatory Considerations

Comments regarding the EPA's regulatory approach submitted by Minnkota Power Cooperative (Minnkota) made in September 2008 (Burns & McDonnell and others, September 2008) appear to have been mostly ignored by the EPA. We encourage the NDDH to make those comments, and the ones in this document, part of the administrative record for the final NOx BACT Determination for the lignite coal-fired utility boilers at Milton R. Young Station. Minnkota, as owner and operator of the lignite-fired cyclone boilers at Milton R. Young Station, is providing these comments as a party subject to the requirements of the Consent Decree (2006).

It is indisputable that there are no SCR installations in operation or planned on units that include cyclone burners firing North Dakota lignite. In fact, to the best of our knowledge, there have been no previously built, and there are not any currently operating, tail-end SCRs installed on full-scale, full-time lignite-fired utility boilers anywhere in the world. This has not been refuted by the EPA or their experts.

The arguments regarding technical infeasibility of SCR technology for the reduction of NOx emissions at M.R. Young Station have been stated previously (BACT, 2006; Minnkota, 2007A, B, C; Burns & McDonnell and others, May 2007;Arfmann and others, August 2007; Burns & McDonnell and others, May 2008; Burns & McDonnell and others, September 2008). Examination of the physical and chemical characteristics of the pollutant-bearing gas stream and comparison to the gas stream characteristics of the source types to which the technology has been previously successfully applied has been presented in detail. The characteristics of cyclone boilers firing North Dakota lignite, whose sodium-rich ash-forming constituents, combined with slagging-type firing methods, create flue gases containing reactive aerosols that are unique. These conditions will cause catalyst fouling, blinding, and poisoning in high-dust, low-dust, and

tail-end SCR configurations. Thus, it has been demonstrated that SCR technology has not been deployed on a "same or similar source type". Accordingly, the NDDH has a reasonable basis upon which to conclude that SCR is not applicable for BACT at Young Station.

Statements of SCR catalyst vendors being willing to guarantee their product resulting from a Burns & McDonnell query and follow-up (Burns & McDonnell and others, April 2007 and May 2008), and subsequent claims by the DOJ's commenter (Hartenstein, July 2008) are based upon the premise that exposure of the catalyst to suitable operating conditions will occur; whether it is possible to achieve such conditions is not their responsibility. Regarding tail-end SCR, one of the queried vendors stated "the fly ash constituents that can poison the catalyst will have been removed from the flue gas stream by the existing ESPs". This statement fails to recognize that submicron aerosols will pass through the electrostatic precipitator (ESP) and further ignores that a wet flue gas desulfurization ("scrubber") system upstream of a tail-end SCR is largely ineffective at removing such aerosols.

The infeasibility of SCR technologies at the MRYS is related to the following issues:

- Cyclone boiler firing characteristics – high temperature slag formation and removal increases production of reactive sodium and potassium rich aerosols
- High sodium lignite contains high levels of organically associated sodium that is prone to form aerosols when fired, especially in slagging-type boilers
- Heat transfer surface configuration required for fuel drying and heat recovery results in high temperature issues for high-dust SCR
- Highly cohesive and reactive sodium rich ash that blinds, plugs, and poisons high-dust SCR catalyst
- ESP and scrubbers do not remove reactive submicron aerosols that blind, plug, and poison low dust and tail end SCR catalyst. No tail-end SCRs have been installed on any full-scale, full-time lignite-fired utility boilers anywhere in the world.

There is no demonstrated evidence that these infeasibility issues have been overcome. Recent literature supports conclusions that high dust, low dust, and tail end SCR are not feasible because of the presence of sodium- and potassium–rich aerosols in the flue gas stream. No SCR catalyst

designs have been developed that can avoid blinding and deactivation by highly-concentrated alkali aerosols in the flue gas. Therefore, it is wrong to assume that SCR systems that have yet to be tested, designed, and proven to be capable of enduring or modifying such challenging flue gas conditions that exist at the units at M.R. Young Station should be considered as technically feasible, without having been successfully installed, operated, and maintained on similar boilers and fuels. It is an invalid response to suggest that Minnkota is required to conduct an extended pilot test program or full-scale experimental construction and testing project for the purposes of supporting a BACT determination, when the EPA's own draft NSR Workshop Manual's definition of a technically feasible control excludes those projects.

EPA's previous comments (U.S. EPA, July 2008) suggest that the BACT decision should turn on cost-effectiveness considerations. This argument puts the cost-effectiveness "cart" before the technical feasibility "horse". The top-down BACT process very clearly eliminates technically infeasible alternatives from the cost-effectiveness analysis. It has been previously demonstrated (Arfmann et al, August 2007) that SCR is—under the definitions provided in the NSR Workshop Manual relating to availability and applicability—technically infeasible in this case. EPA's suggestion that the hypothetical application of a technically infeasible technology could potentially be a cost-effective emissions control method that constitutes BACT is at odds with the NSR Workshop Manual.

The EPA and the DOJ's commenter continue to argue that this is a case where hypothetical full-scale or demonstrated pilot-scale SCR technology performance data must be quantified for a BACT analysis in order to refute the EPA's position that SCR is technically proven for NOx reduction on all fossil fuels, not excluding North Dakota lignite, while ignoring the severe pore plugging documented for the Coyote Station pilot SCR catalyst testing experience (Benson and others, 2005) along with boiler firing method-specific and fuel-specific technical reasons for the technology's infeasibility.

Corrections, Clarifications and Omissions of Hartenstein's Remarks

The DOJ commenter's (Hans Hartenstein's) October 2008 remarks need to be clarified and corrected for the administrative record.

RESPONSES TO GENERAL REMARKS:

1. The lack of catalyst deactivation data for high-dust, low-dust, or tail-end SCR technology, if it were to be applied to the boilers at MRYS, supports the argument that an extended pilot test program or full-scale experimental construction and testing projects would need to be conducted in order to compare with other pilot-scale or full-scale catalyst experience on cyclone boilers firing other coals before confirmation of technical feasibility can be confirmed. It is erroneous to assume that the fine sodium sulfate aerosols in MRYS boiler flue gas that will deactivate SCR catalyst will be sufficiently removed by the ESP and wet scrubber systems upstream of a tail-end SCR, and therefore are unlikely to pose a rapid deactivation threat. ESPs and wet scrubbers are not highly efficient at removing fine submicron particles and aerosols that contain high levels of sodium, potassium, and sulfuric acid (Buecker 2008; Ohlstrom and others, 2006, Hurley and Katrinak, 1992). These submicron species have been shown to penetrate the micropores of the catalyst by diffusion processes, as previously described by EERC (Benson and others, 2005; Minnkota 2007A, B, C; Burns & McDonnell and others, April 2007, May 2007, May 2008, September 2008; Arfmann and others, August 2007).

   Recent work conducted by Zheng and others (2008) described the diffusion of aerosols and their ability to cause catalyst poisoning. These efforts followed earlier studies where Zheng and others (2005) found that biomass derived alkali rich aerosols caused a drop in NOx reduction activity by 52% after about 1140 hours of operation. SCR vendors were specifically requested (Burns & McDonnell, April 2007, May 2008) to provide data that would support the EPA's arguments that high-sodium North Dakota lignite would not be infeasible for full-scale, full-time cyclone boiler SCR applications. The details of any estimates of catalyst life and deactivation rates offered by vendors were not made available for review.

2. Hartenstein remarked that because Burns & McDonnell's SCR Consultant (Tackticks) did not actually state that SCR is technically infeasible at Milton R. Young Station, that their opinions do not support this same conclusion expressed by B&McD and EERC. Hartenstein has drawn this conclusion without recognizing the arguments Tackticks made that correspond to the previously stated position and interpretation (Arfmann and others, August 2007) of "technical feasibility" as described in the EPA's 1990 NSR Workshop Manual. It is our collective position, based on valid arguments provided by Minnkota, Burns & McDonnell, Steve Benson, Volker Rummenhohl, and several SCR system suppliers, that successful application of SCR technology on this fuel at this powerplant has not been sufficiently demonstrated by actual relevant pilot- or full-scale experience to confirm its technical feasibility as stated previously with our interpretation of the definition of those terms.

   Volker Rummenhohl was responsible for the process design of 26 tail-end and 7 low-dust SCRs with re-heat systems. The first one started in Germany in 1987, and the last ended in 2008 (but was not subsequently approved for implementation). Mr. Rummenhohl was also responsible for the commissioning of ten tail-end SCRs and the O&M performance of six tail-end and one low-dust SCRs with reheat.

   We agree with Volker Rummenhohl that it is extremely imprudent to apply SCR to a utility boiler with such differences in firing type and fuel burned compared to those situations that have been proven successful without first performing extensive pilot testing and achieving acceptable results, followed by confirming the feasibility of the full-scale design. One cannot look just at the bulk flyash loading and average concentrations of the trace elements and other poisons in the fuel to decide whether SCR technology will work. It is incorrect to make a blanket statement such as made by Hans Hartenstein in his October 2008 remarks that implies it is always feasible to install TESCR.

RESPONSES TO SPECIFIC COMMENTS:

1. EERC has provided detailed information that explains why SCRs are not able to tolerate the higher levels of alkali species, especially in aerosol form, contained in flue gas such as that exhausted from the MRYS boilers as compared to PRB coal-fired boilers that have applied

high-dust SCRs. Hartenstein incorrectly states that Coyote pilot-scale SCR testing in a high-dust configuration does not "properly represent the types of deactivation mechanisms or the rate of catalyst deactivation that can be expected in a TESCR".

As described previously, fly ash produced upon combustion ranges in size from submicron aerosols to particles greater than 10 μm. The very small sodium and potassium enriched particles diffuse into the pore of catalyst no matter if it is low-dust or tail-end SCR catalyst causing rapid plugging, blinding, and deactivation. These small particle are very cohesive and reactive. EERC has described the fine particulate and aerosols released from cyclone boiler combustion are especially enriched with sodium and potassium sulfates and other compounds when generated from firing North Dakota lignite. Combustion of North Dakota lignite in the cyclone-fired boilers at Milton R. Young Station promotes the vaporization of sodium and potassium and the production of submicron particles and aerosols through homogeneous condensation of the vaporized species. These fine materials, which are comprised of highly-concentrated sodium and sulfur containing compounds, are entrained in the flue gas stream. Submicron particles and aerosols are not effectively removed from the gas stream by the high-efficiency electrostatic precipitators nor by wet lime-based flue gas desulfurization systems (scrubbers).

SCR catalyst can be become ineffective in the following ways:

- Plugging channels by so called "popcorn ash" or in many cases typical of ash deposits fragments. Channel plugging is largely driven by the size of the ash materials carried back into the system and can be controlled by the use of screens to remove the ash or larger pitch catalyst.
- Masking of the surface by a dense phase. The phases that form are typically sulfates that cause bonding of other particles (silicates and aluminosilicates) on the surface. The sulfates have formed as a result of in situ sulfation of deposited alkali and alkaline earth materials.
- Diffusion of small particles and aerosols into the pores of the SCR blocking the diffusion of NOx and ammonia to the active sites.

- Poisoning of the active sites in the catalyst by the diffusion of various types of reactive aerosols such as those rich in sodium and potassium. The aerosols will diffuse into the pores and react with the active components of the catalyst.

The latter two mechanisms do not rely on the bulk loading of flyash present in the gas stream. While the majority of the bulk flyash mass will have been removed by the upstream ESP and wet FGD scrubber for a tail-end SCR, there will still be a large number of very small and reactive particulate and aerosols that will severely affect the catalyst. Because these residual aerosols and fine particulate are not totally removed by the upstream gas treatment equipment, they are not negligible as the DOJ's commenter suggests.

As Volker Rummenhohl (see Appendix A) and others have stated in the cited references, the concentration of certain elements such as alkali and other species (arsenic and sulfuric acid aerosol), do not have to be large in magnitude before they will cause significant catalyst deactivation or become visible. In cyclone-fired system the ash is partitioned between fraction that leaves the cyclone with the bulk gas flow and the materials that are retained in the slag. The fraction leaving the cyclone with the hot gases are enriched in fine particulate and vapors that will have high levels of flame-volatilized species such as sodium, potassium, and sulfur relative to the molten slag. The molten slag-related has a higher abundance of lower volatility material. The fly ash is enriched in the volatile elements that are in the form of submicron particles and aerosols. The submicron particles and aerosols are not removed sufficiently by an ESP and wet scrubber to eliminate their blinding, plugging, and deactivation tendencies for SCR catalyst in a TESCR configuration. The removal efficiency for fine particles and aerosols less than 1 μm (micron) is documented in EPA's report entitled "Stationary Source Control Techniques Document for Fine Particulate Matter" (Woodward, 1998). The authors reported the following on page 209: "Most conventional scrubbers can achieve high collection efficiencies for particles greater than 1.0 μm in diameter, however they are generally ineffective collection devices for submicrometer (<1 μm) particles."

2. The main power boiler with an SCR (Unit 2) at the Avedore utility powerplant mentioned by Hartenstein (Hartenstein, October 2008) is a multiple-fuel fired system, and is not continuously fired with 100% biomass as may be implied. A smaller Avedore boiler

associated with Unit 2 is fired with 100% wood pellets and/or straw biomass, which does not exhaust its flue gas through any SCR. The main boiler's flue gases are significantly dominated by the main fuel, which can be natural gas, heavy fuel oil, or bituminous coal. The SCR for the main boiler is exposed to a reduced concentration of co-fired wood biomass-related emissions. The first bar graph in the cited reference presentation (Noppenau, 2006) shows that 100% natural gas was fired for three continuous months (July, August, September), and straight fuel oil was fired during the three winter months (January-March). It appears that wood pellets were co-fired with fuel oil during April-June and October-December. So the catalyst exposure to biomass-related flue gases at Avedore is not as drastic as Hartenstein implied.

According to the catalyst washing technical presentation paper by Haldor Topsoe (White, 2007) cited by Hans Hartenstein, the main boiler's SCR catalyst at Avedore Unit 2 has required rejuvenation nine times and replacement once within the first 30,000 hours of operation. When reviewed in combination with the other paper (Noppenau, 2006), it is apparent that a significant portion of the annual operating time for the main Avedore Unit 2 boiler does not involve co-firing of biomass. Based on the data provided, the actual rate of catalyst deactivation could be much more significant than the above numbers imply. Substantial, rapid deactivation is indicated, requiring catalyst maintenance activities on the order of approximately every 1000 hours of estimated biomass co-firing operation.

Volker Rummenhohl considers this frequency of catalyst washing excessive, and believes this is not indicative of a successful SCR installation. Of course, catalyst vendors and other companies provide catalyst washing services, so this is good for such businesses. Mr. Hartenstein himself has been employed as the president of such a company (Hartenstein, July 2008), so his opinion on this subject may be influenced by his previous personal involvement.

3. Hartenstein discounts the silicon tetrafluoride blinding problems from firing bituminous coal in certain German utility TESCRs as isolated and very short in duration. Volker Rummenhohl was in charge of the investigation of this phenomena and it was very serious for the supplier and utility (Steag) that was experiencing the rapid catalyst deactivation. If

rapid TESCR blinding and decreased removal performance were to occur at a site such as MRYS, the 30-day rolling average emission requirements would still need to be met continuously.

4. Hans Hartenstein repeats what one catalyst vendor said (Burns & McDonnell and others, May 2008): that the Coyote Station SCR slipstream pilot testing demonstrated that 6 mm pitch catalyst is not suitable for a high-dust SCR application featuring highly adhesive flyash. At least one important point can be made from these and other situations showing rapid catalyst deactivation. The published experience base for catalyst designs suitable for coal-fired boiler applications or coal additives that are available and been proven to tolerate or alleviate the severe blinding and plugging of the catalyst pore structure due to the high levels of sodium-rich aerosols present in flue gases derived from the cyclone-fired combustion of ND lignite is extremely small. As EERC has stated in previous comments, catalyst exposed to sodium sulfate aerosols are subject to the same blinding and deactivation mechanisms regardless of catalyst pitch.

   The most important catalyst deactivation mechanism to recognize is diffusion of aerosols into the pores of the catalyst followed by reaction of the alkali (sodium and potassium) with active sites in the catalyst and/or the reaction of gas phase SO_2 and SO_3 to produce sulfates and pyrosulfates. Recently testing was conducted by Strege and others (2008) at a stoker-fired utility boiler firing a blend of biomass and Powder River Basin coal (PRB) using the same reactor that was used at the Coyote Station. The main difference in the recent testing as compared to the Coyote tests was that the nozzle normally used to isokinetically extract the flue gas was pointed in the same direction of the gas flow to minimize the extraction of large particles from the flue gas stream into the reactor. The exposed catalyst was tested for reactivity and they found that the catalyst deactivation rate was about 18% per 1000 hours. The components responsible for the deactivation were sodium, potassium, and calcium sulfate based materials. Alkali components (sodium and potassium) were found deep inside the pores of the catalyst.

5. The abundance of sodium and other ash forming components vary dramatically in various types of biomass cited as examples of similarity to North Dakota lignite-fired cyclones

relative to SCR applications. The typical levels of ash and sodium in typical wood as co-fired in power boilers is lower than the range indicated in the comparison table provided in Mr. Hartenstein's October 2008 remarks. The amount and form of alkali species in the coal along with combustion processes influence their ability to be enriched in the aerosol and fine particle fraction of the fly ash. The size and composition of the particle along with gas velocity determines their ability to penetrate and deposit on SCR catalyst passages and in pores and cause plugging, blinding, and poisoning.

6. Hartenstein did not refute the formation of aerosols or the mechanism of partitioning between the slag and fly ash components in cyclone-fired systems that result in an enrichment of sodium and other flame-volatilized species in the flue gas.

7. Hartenstein apparently agrees that penetration of alkali-rich aerosols in the flue gas from high sodium Fort Union (North Dakota lignite) coals fired in cyclone-fired boilers into the pores of SCR catalyst will cause significant blinding and poisoning in high dust SCR applications. He also seems to believe that this will not be the case for tail-end SCR applications, which he assumes will see flue gases cleaned and scrubbed of harmful elements removed by the upstream treatment equipment.

8. Hartenstein's discussion did not include statements of catalyst vendor guarantee experience associated with European coal-fired utility boilers cofiring high alkali (Na and K) containing biomass. Based on recent contacts, Volker Rummenhohl has learned that many catalyst vendors are reluctant or unwilling to guarantee catalyst performance in such applications.

9. There is conflicting information regarding the startup date of the tail-end SCR at Rudow Unit 2 (Fisia Babcock, IEA Coal Research). The important issue to understand is that the contract to retrofit a TESCR on the Rudow unit was signed prior to 1990, it fired bituminous coal, not lignite, and was placed into cold standby in 1998 (and has since been decommissioned). Assuming the execution of the project was delayed until completion occurred in 1994, it does not change the fact that no other tail-end SCRs have been designed and installed for operation on coal-fired utility boilers for more than a decade, either in the United States or Europe.

10. The statement that the Walsum Unit 7 boiler burning bituminous coal cited in previous comments (Burns & McDonnell et al, September 2008) as operating with a LDSCR, not a TESCR, was not refuted by Hans Hartenstein; the remarks indicate this unit not being cyclone-fired is also debatable, as there are other references that indicate the unit employs cyclone burners.

11. Out of the hundreds of European SCRs installed on coal-fired power plants, experience at lignite-fired utility boilers has been very limited and dissimilar to the conditions at Milton R. Young Station. One high-dust SCR installation was at Voitsberg Unit 3 (Austria) and there were HDSCRs on three units at the Bayernwerk Schwandorf plant in Germany. These units were not slagging-type (cyclone-fired), the fuel burned was much lower in sodium and other alkali elements than contained in North Dakota lignite. These units are no longer in operation.

Conclusions

In the end, EPA's objections to NDDH's Preliminary BACT Determination may be reduced to disputing NDDH's characterization of the gas stream characteristics and the impacts of those characteristics on boiler and emissions control operations. EPA and Hartenstein suggest that these impacts can be resolved by the use of TESCR, and that TESCR technology will work at MRYS (July, 2008). We believe their arguments are flawed because they fail to recognize the significance of these facts:

- There is no prior experience with full-scale SCR of any type on any utility boiler firing North Dakota lignite.
- Results from the only known example of simulating SCR catalyst exposure to high-alkali containing flue gases produced from firing North Dakota lignite in a cyclone boiler showed severe, rapid catalyst blinding and plugging due to sodium and potassium rich species (Benson and others, 2005). The Coyote pilot-scale SCR test was intended to evaluate the fouling potential of SCR on lignite coal. It was developed by a consortium

of three catalyst vendors, EPRI, U.S. DOE, and other participants that design and install SCR systems as well as end-user utilities that have applied SCR on their boilers. This experience demonstrated the generation of alkali-sulfate compounds that plugged every micropore of the test catalyst when examined under a scanning electron microscope. This catalyst blinding and plugging was so severe that the catalyst vendor who supplied it was unwilling to analyze it for deactivation.

- European SCR experience at lignite-fired utility boilers has been very limited and dissimilar to the conditions at Milton R. Young Station. One high-dust SCR installation was at Voitsberg Unit 3 (Austria) and there were HDSCRs on three units at the Bayernwerk Schwandorf plant in Germany. These units were not slagging-type (cyclone-fired), the fuel burned was much lower in sodium and other alkali elements than contained in North Dakota lignite. These units are no longer in operation.
- There has never been, to the best of our knowledge, any tail-end SCRs applied to coal-fired utility boilers burning lignite in Europe. There have been no full-scale TESCRs downstream of a wet FGD scrubber and electrostatic precipitator installed on any coal-fired utility boilers in North America (see Appendix A). Aerosols will still get through the ESP and wet FGD scrubber, so catalyst deactivation problems will occur similar to or worse than those experienced by SCRs fitted to boilers co-fired with large amounts of alkali-producing biomass. We do not know if these problems will be successfully solved.
- The gross amount of ash, and specifically the sodium and potassium fraction of the lignite coal ash, is not relevant to whether low-dust or tail-end SCR catalyst will become rapidly plugged, blinded, and deactivated. Combustion of North Dakota lignite in the cyclone-fired boilers at Milton R. Young Station promotes the production of submicron particles and aerosols. These fine materials comprised of highly-concentrated sodium sulfate, are produced from the condensation of flame volatilized species and are entrained in the flue gas stream. Submicron particles and aerosols are not effectively removed from the gas stream by the high-efficiency electrostatic precipitators nor by wet lime-based flue gas desulfurization systems (scrubbers).
- Statements of SCR catalyst vendors being willing to guarantee their product resulting from a Burns & McDonnell query and follow-up (2007, 2008), and subsequent claims by

the DOJ's commenter (July 2008) are based upon the premise by these vendors that exposure of the catalyst to suitable operating conditions will occur; whether it is possible to achieve such conditions is not their responsibility.

- There can be no substantiated basis established such that the performance and longevity of such hypothetical solutions could be estimated without performing extensive pilot scale testing that proves that SCR catalyst can avoid blinding and deactivation by the alkali aerosols in the flue gas, and developing detailed designs of workable, effective solutions to the existing conditions. It is wrong to assume that SCR systems that have yet to be tested, designed, and proven to be capable of enduring or modifying such challenging flue gas conditions that exist at the units at M.R. Young Station should be considered as technically feasible, without having been successfully installed, operated, and maintained on similar boilers and fuels. It is an invalid response to suggest that Minnkota is required to conduct an extended pilot test program or full-scale experimental construction and testing project for the purposes of supporting a BACT determination, when the EPA's own draft NSR Workshop Manual's definition of a technically feasible control excludes those projects.
- Because of the unique boiler configurations and firing characteristics employed by these boilers and the fuel they burn, there is no substantive certainty of how all the documented temperature issues for high-dust SCR and the submicron aerosols and flue gas conditions for any SCR configuration, would be favorably resolved for the boilers at MRYS. As far we are aware, there have been no high-dust SCRs installed on cyclone-fired boilers that have the kind of fuel drying and heat recovery systems employed at MRYS.
- Volker Rummenhohl is an experienced SCR process design engineer who has been responsible for the process design of 26 tail-end and 7 low-dust SCRs with re-heat system. Volker has stated, and we concur, that it is extremely imprudent to apply SCR to a utility boiler with such differences in firing type and fuel burned compared to those situations that have been proven successful without first performing extensive pilot testing, achieving acceptable results, followed by confirming the feasibility of the full-scale design. One cannot look just at the bulk flyash loading and average concentrations of the trace elements and other poisons in the fuel to decide whether SCR technology will

work. It is incorrect to make a blanket statement such as made by Hans Hartenstein in his October 2008 remarks that implies it is always feasible to install TESCR.

- Based upon all the evidence presented to date, it is technically infeasible to apply any form of SCR technology (high-dust, low-dust, or tail-end SCR) to the lignite-fuel cyclone-fired boilers at the Milton R. Young Station.

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APPENDIX A

Volker Rummenhohl's Report
"Catalyst Poisoning"

Catalyst Poisoning

By

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Fuel Tech, Inc.

November 17, 2008

Selective Catalytic Reduction (SCR) Catalyst can be rapidly deactivated (poisoned) by fuel impurities. Some of these impurities are present at trace levels. These impurities can either plug the pores physically or react with the active centers in the pores chemically on a permanent basis and reduce the number of active cells. The impurities can interact with the catalyst in three phases: solid, liquid, and vapor (gas). Many trace elements such as arsenic (As), selenium (Se), lead (Pb), cadmium (Cd), antimony (Sb), and other more abundant elements, such as sodium (Na), potassium (K), and phosphorus (P) will vaporize during combustion and condense on the surfaces of larger entrained particles or be emitted as elemental aerosols. The larger solid trace element-containing particles are too large to penetrate the pores. They will remain on the surface of the catalyst and are neutral regarding the activity, but may mask or blind the pores so that ammonia and NOx molecules cannot reach the active sites to react. Particulate loading is not of concern when the cause of the catalyst deactivation is due to aerosols. The aerosols are less than a micrometer in diameter and can be in a liquid or solid state. The condensed aerosols can penetrate into the pores of the catalyst by diffusion processes and can accumulate and react within the catalyst, plugging and poisoning active sites. In addition, trace elements in a liquid solution can further penetrate the pores.

In Minnkota's case, major elements such as sodium and potassium produce aerosols and liquid phase mixtures that will blind and poison catalysts. As previously discussed by EERC, combinations of sodium-potassium-pyrosulfate salts can have liquid (i.e. melting point) temperatures as low as 535°F. Submicron sodium- and potassium-rich aerosols penetrate catalyst pores and cause physical plugging of the catalyst pores and poisoning of the active sites. Arsenic in bituminous coal is an example of a well-known catalyst deactivation mechanism involving a trace element in vapor form that penetrates the micropores, reacts with the active sites during SCR operation, and causes rapid deactivation by permanently poisoning the catalyst.

The relevant catalyst poisons in the case of MYRS are sodium and potassium. Both elements are known catalyst poisons in case biomass is co-fired with the primary fuel in utility boilers[1]. Since widespread use of biomass co-firing in utility power boilers equipped with SCR catalysts is relatively recent, specific published knowledge of the successful methods of avoiding or mitigating the negative effects on SCR catalyst deactivation is limited. For this reason, we will use arsenic as an example to demonstrate catalyst vendors' initial lack of awareness and the subsequent understanding of the deactivation mechanism.

The application of SCR technology to utility boilers was first performed in 1975 on a utility boiler in Japan. The second country using the technology on powerplants was Germany. It started in the mid 1980s with demonstration and pilot plants. Arsenic was not known to be a catalyst poison at that time. One German utility insisted on a pilot plant despite the fact that all Japanese catalyst licensors were willing to provide all guarantees without pilot testing. The result of the pilot test in the power station Franken was that the catalyst supplied by four different suppliers significantly deactivated in 200 hours due to arsenic poisoning. Since this occurred, there has been significant and lengthy investigations, pilot and full-scale catalyst testing at utility powerplants and product development to identify causes and solutions[2].

Arsenic in a gaseous form is a strong catalyst poison. The critical concentration of gaseous arsenic trioxide (As_2O_3) is 10 $\mu g/Nm^3$. Almost all catalyst suppliers have this standard. The suppliers add catalyst volume to meet guarantees when the concentration of arsenic trioxide in the flue gas entering the SCR reactor is between 10 and 50 $\mu g/Nm^3$. Longevity of catalyst exposed to an arsenic concentration over 50 $\mu g/Nm^3$ in the flue gas at the inlet of the SCR will not be guaranteed by the catalyst supplier without subsequent arsenic mitigation as described below.

The art of the catalyst design in such cases is to decide how much gaseous arsenic will be in the flue gas based on the fuel specification. In one case, a high sulfur bituminous coal contained 30 ppm As by weight in the coal. This would result in 3850 $\mu g/Nm^3$ if all fuel arsenic would become gaseous. This demonstrates that a very small fraction of the fuel arsenic – less than 0.1 ppm by weight for bituminous coal, is the limit for SCR operation without problems.

There are several factors determining the amount of gaseous arsenic that is produced during combustion of arsenic-containing coal. The free calcium oxide (CaO) content in coal is the most important factor. Calcium binds arsenic in the solid form [calcium arsenate, $Ca_3(AsO_4)_2$]. German experience showed that if the free CaO concentration in the fuel is above 2 to 2.5% by weight of the ash, arsenic is not a problem for the catalyst. Addition of limestone into the furnace (boiler combustion zone) is required if the free CaO in the fuel is insufficient to prevent arsenic poisoning of the catalyst.

The sulfur content of the German bituminous coals involved with arsenic catalyst poisoning was approximately 1% by weight. Experience in the U.S. demonstrated that the free CaO concentration must be higher if the sulfur content is higher. The reason for this is the increased amount of sulfur trioxide (SO_3) found in the furnace. SO_3 reacts faster with CaO than arsenic does, so the sulfur binds with the available calcium preferentially, leaving less for binding with arsenic.

Other factors in the formation of gaseous arsenic are furnace temperature, burner type, total excess air and chlorine concentration. "Arsenic-resistant" catalyst has been developed by making the catalyst surface inactive to arsenic oxide, and by modification of the active sites. Because of the abundance of calcium in North Dakota lignite, catalyst

deactivation due to arsenic poisoning is not likely to be significant if SCR technology in such cases were not technically infeasible for other reasons. The reasons for technical infeasibility of SCR technology on North Dakota lignite-fired boilers are because of the sodium, potassium, sulfur, and other elements that will be present in aerosol form in the flue gas and rapidly deactivate the catalyst.

Most coals commonly fired in utility boilers do not contain the high levels of sodium as North Dakota lignite, and the fuels that do have significantly high alkali contents are not typically fired in boilers that are fitted with SCRs. The same extensive knowledge and operating experience that exists for bituminous coal that may cause arsenic poisoning of SCR catalyst and the means of preventing its negative effects does not exist for the formation of gaseous or aerosol forms of sodium and potassium. Two catalyst suppliers, Argillon and CERAM, provided a brief response to general questions seeking information about their experience with sodium and potassium concentrations that would be of concern for causing accelerated catalyst deactivation. The vendors' responses show that both companies don't know how high the gaseous sodium and potassium concentrations can be to ensure proper catalyst performance.[4,5]

In Mr. Hartenstein's remarks dated October, 2008, in the second paragraph of page 4: "Initially, isolated events of silicon tetra fluoride (SiF_4) blinding in bituminous coal-fired units were reported, but persisted only for a very short period of time." His reference for this statement is personal discussions with plant personnel.

Volker Rummenhohl was the project manager for the project to find the cause and solution for 50% catalyst deactivation in 2,000 hours in tail-end SCRs resulting from unknown reactions. The president of STEAG (today, the company is known as Evonik) used to start meetings about this matter with the statement: "We must find the reason and a solution. The company will be at risk if not." It took more than two years to find the reason and implement the solution. It also took several million dollars for research and implementation. It was also not isolated. All six STEAG tail-end SCRs were impacted.

Up to that point, it was generally accepted that tail-end SCR catalyst would not rapidly deactivate because of all the flue gas cleaning taking place in the upstream electrostatic precipitator would remove practically all the significant dusts and flue gas desulfurization systems would remove a high percentage of the sulfur dioxide. The cause of the rapid TESCR catalyst deactivation turned out to be silicon tetrafluoride. Silicon (introduced as part of the coal ash) reacted with hydrogen fluoride (HF, produced during combustion) and condensed sulfuric acid (H_2SO_4) on the plates of the FGD gas/gas heater (GGH) to form silicon tetrafluoride (SiF_4). SiF_4 at the TESCR operating temperature is gaseous and therefore penetrated the pores of the catalyst[3]. This was completely unexpected. Everyone assumed an extremely long catalyst lifetime for a catalyst in a tail end plant.

Besides the catalyst issues, other equipment issues can impact the feasibility of a tail-end SCR. In a project in Wisconsin, the owner has been forced to change from a tail-end to a low-dust SCR design for those other reasons. Differences to German tail-end

applications were the much higher SO_2 removal efficiency requirements of the Wisconsin plant's wet FGD scrubber and the fact that the plant is a "zero-discharge" site.

Mr. Hartenstein refers to the catalyst case history at Avedore Power Station in Denmark as indicative of successful catalyst performance on a biomass fired boiler. Two presentations [6,7] have been mentioned that provide relevant information on the plant operation. Close examination of those and other references previously mentioned by UND refute Mr. Hartenstein's point that SCR catalyst will be effective on units with sodium, potassium and other elements present as an aerosol in the flue gas.

It should be noted that the referenced Avedore unit that uses SCR technology is not a 100% biomass fired boiler, as stated in Mr. Hartenstein's October 2008 remarks and in the referenced catalyst washing presentation by Haldor Topsoe. The boiler fires natural gas and other fuels. The referenced Elsam presentation does not show that the flue gas from the small, biomass fired boiler is mixed with that of the larger boiler prior to the SCR system. The smaller boiler does not exhaust its flue gas through any SCR.

In addition, it is noted in the referenced Haldor Topsoe catalyst washing presentation that the entire catalyst loading on Avedore Unit 2 was replaced after 30,000 hours of operation. During the initial 30,000 hours of operation, the catalyst was washed nine times. This frequency of catalyst washing is excessive and not indicative of a successful SCR installation. The Elsam presentation includes a bar graph for "fuel combination – 12 month" and "fuel combination - 24 hours –April" that show that cofiring wood with heavy fuel oil (50:50 ratio) during April was only 25% of the total fuel, and apparently co-firing occurred during only half (12 hours) of the daily operating time. If the boiler were continuously co-fired with wood 24 hours per day year-round, we would expect this catalyst to show a rapid, severe decline in catalyst activity.

The referenced H-T presentation shows a graph of catalyst relative activity versus time includes Avedore Unit 2's catalyst exposure time when no biomass cofiring occurred. "Line B" in the presentation represents "average wood-fired high dust catalyst deactivation" over time. This graph is misleading, as it shows a linear decay in catalyst activity for Avedore Unit 2's biomass co-firing experience compared with a linear curve fitted to data for "average coal fired, high dust deactivation". "Line B" on the graph is also misleading in that it does not show the cyclic effects of deactivation and washing on catalyst activity for the biomass case until it reached 90% deactivation in 30,000 hours.

It is interesting that Hans Hartenstein portrays the catalyst vendors as willing to guarantee performance on coal-fired utility boilers that co-fire biomass (or plan to do so). Meetings and discussions with all of the catalyst vendors except one reveal great reluctance or refusal to offer such guarantees.

Hans Hartenstein mentioned Marl as an example of TESCR without an FGD gas/gas heater upstream of the induced draft fans following a wet scrubber. It does, however, use scrubber bypass gas to reheat the scrubber outlet gas above saturation. Marl is not on the official Evonik website. Maybe Mr. Hartenstein can explain whether it is a waste

incinerator or boiler. Mr. Hartenstein should have this information since, based on his email address used in communicating with the SCR catalyst vendors, he is obviously an employee of Evonik. He also claimed that a plate-type gas/gas heat exchanger from Balcke-Durr was used in the Marl plant. A look at Balcke-Durr's internet website indicates they have discontinued this product and are now offering a rotary (e.g. Ljungstrom)-type instead.

Another plant that has a "wet" booster draft fan following a wet scrubber with an FGD gas/gas heater before a tail-end SCR is Herne. When asked if he would ever want to see this arrangement repeated, the plant engineer at Herne said "never in his lifetime".

This brings me to Hans Hartenstein's credibility problem. He has absolutely zero hands-on experience with tail end SCRs on utility boilers. It is very clear that statements made by Hans Hartenstein about the feasibility of tail-end SCRs on utility boilers burning North Dakota lignite are personal opinion and are not based on relevant technical expertise in this field.

Volker Rummenhohl was responsible for the process design of 26 tail-end and 7 low-dust SCRs with re-heat systems. The first one started in Germany in 1987, and the last ended in 2008 (but was not subsequently approved for implementation). Mr. Rummenhohl was also responsible for the commissioning of ten tail-end SCRs and the O&M performance of six tail-end and one low-dust SCRs with reheat.

It is extremely imprudent to apply SCR to a utility boiler with such differences in firing type and fuel burned compared to those situations that have been proven successful without first performing extensive pilot testing and achieving acceptable results, followed by confirming the feasibility of the full-scale design. One cannot look just at the bulk flyash loading and average concentrations of the trace elements and other poisons in the fuel to decide whether SCR technology will work. It is incorrect to make a blanket statement such as made by Hans Hartenstein in his October 2008 remarks that implies it is always feasible to install TESCR.

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