SCR Experience with High CaO Coals

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Abstract

With environmental pollution on the increase in China, steps are being taken by the government as well as individual businesses to help clean the air. From the land comes a vast abundance of coal to be burned and turned into much needed electricity to drive the economic machine that is China. However, this burning of the fossil fuel coal comes with the threat of NOx emissions. Selective catalytic reduction (SCR) is the most effective technology to reduce NOx from stationary sources such as the many coal fired power plants dotting the nation. And with the indegenous coals being burned comes new challenges to designers of SCR systems, specifically the effects of CaO in the ash and high dust loading.

CaO Experience

Cormetech has vast experience when dealing with a myriad of design parameters in the United States and abroad. From designing SCR catalyst for the utility baseload in America that burns numerous kinds of fuels to designing intricately formulated compositions for the refinery industry, Cormetech's wealth of experience broaches the entire spectrum of fuel compositions.

Coal is the most abundant and most utilized resource in the world for the production of electricity. The four basic types of coal are anthracite, bituminous, sub-bituminous and lignite. Anthracite is very rarely used in utility boilers for the purpose of creating electricity, while bituminous and sub-bituminous are most popular. Each of these coal types have their own special properties and chemical compostitions. These compositions and the specific usage in boilers are integral to the design a SCR catalyst that will accomplish the guaranteed performance of the system.

The fly ash produced from the burning of pulverized coal in a coal-fired boiler is a fine-grained, powdery particulate material that contains calcium oxide. Calcium oxide (CaO), commonly known as lime, quicklime or burnt lime, is a widely used chemical compound. It is a white, caustic and alkaline crystalline solid. This fly ash is carried off in the flue gas downstream to the SCR catalyst beds.

Early experience was limited to lower CaO coals. The ash content typically was 16% weight of the coal while the CaO content was approximately 6% weight of the ash produced.

Plant	Start-Up (Year)	Ash (% wt)	CaO in Ash (% wt)	Location	Source
A	1983	13.5	3.9	Japan	MHI
B	1980	15.8	4.6	Japan	MHI
C	1984	11.9	3.0	Japan	MHI
D	1991	11.5	3.7	Japan	MHI
E	1983	14.1	4.3	Japan	MHI
F	1991	9.1	4.5	Japan	MHI
G	1989	11.0	6.0	Japan	MHI
H	1991	11.6	3.5	Japan	MHI
I	1990	10.1	2.8	Japan	MHI
J	1988	9.0	4.0	Germany	STEAG
K	2003	12.3	4.4	France	Alstom

Table 1: Early Coal Experience

Arsenic poisoning was the primary catalyst deactivation mechanism with these lower CaO coals and the presence of CaO might actually extend the catalyst life by mitigating the impact of the arsenic (lime injection).

Recent experience in the United States has seen an increase in the use of Powder River Basin (PRB) coals that are mostly mined in the state of Wyoming. The ash content ranges from 4% to 10% in the coal while the CaO content ranges from 8% - 30% in the ash. PRB coals typically have 2 to 3 times the effective CaO of historical coal experience.

Plant	Units	Ash (% wt)	CaO in Ash (% wt)	Install Date / Comments
A	2	5.3 – 9.8	18.0 – 26.3	2000 – 2001
B	3	5.1 – 5.4	16.5 – 18.0	2001 – 2003 (80% PRB)
C	2	4.9	20.4	2002 – 2003
D	1	6 – 7	21.3	2003
E	4	4.4 – 9.4	20.0 – 28.7	2003 / 2003 / 2005 / 2005
F	2	6 – 8	8 – 13	2003 – 2004
G	3	7.0	11.0	2003 / 2003 / 2007 (65% PRB)
H	2	5.0	23.2	2003 / 2006
I	1	4.4 – 6.3	20.4 – 24.5	2004
J	1	3.7 – 7.5	16.6 – 32.6	2007
K	1	4.4 – 7.2	16.1 – 26.1	2007

Table 2: Cormetech's United States recent experience - PRB Units

Within China, the coals examined to date have significantly higher amounts of CaO. Data gathered from coal specifications show an ash content range of 9% to 24% while the CaO content ranges from 13% - 30% in the ash. Due to the high ash content, the high CaO coals in china have a higher effective CaO than typical PRB Coals. While other catalyst poisons (Na, K, P, As) still exist, calcium sulfate ($CaSO_4$) masking becomes the primary catalyst deactivation mechanism caused by high CaO coals.

The CaO deactivation mechanism can be explained by the CaO primarily being caught on the catalyst surface where this process is dependent on availability and adhesion of the CaO. Once the CaO is caught on the surface, SO_3 bonds to the CaO and diffusion takes place. This process is a function of mass transfer and concentration. A tertiary step is the diffusion and expansion of CaO and SO_3 forming the $CaSO_4$. This reaction is a function of diffusion rate and SO_3 concentration. Particle expansion is ~14%. The last step in the mechanism is the deactivation of the catalyst where NH_3 and NO_x cannot reach the active sites being masked by the $CaSO_4$.

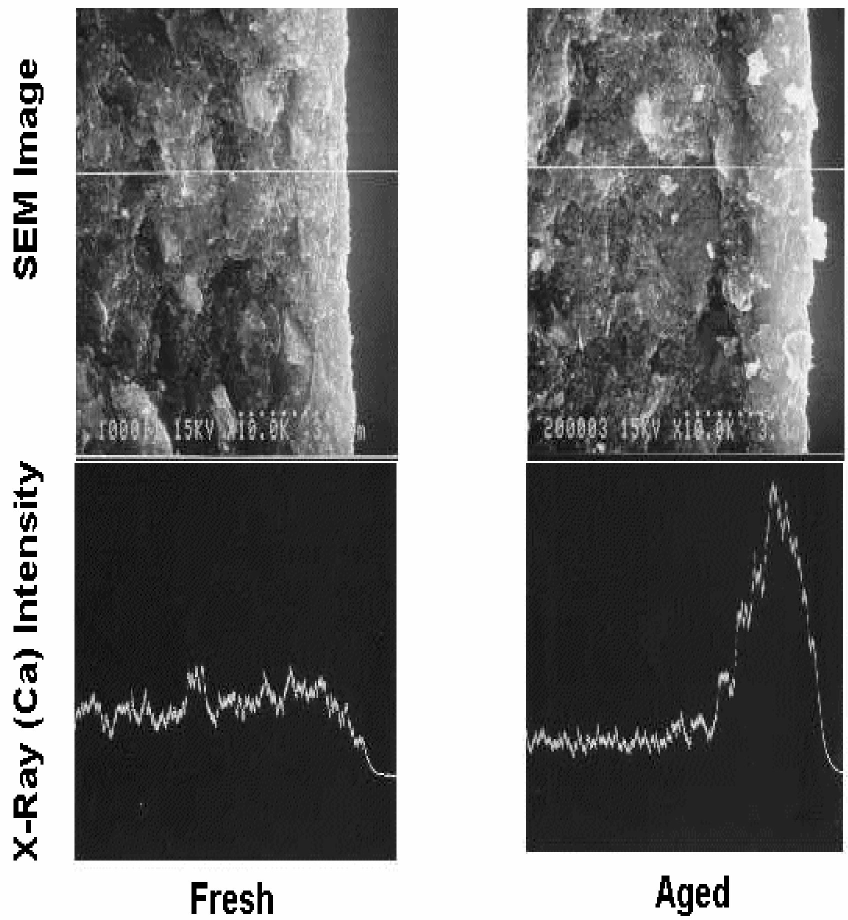


Image 1: CaO Deposition and CaSO4 Masking
Images captured by a scanning electron microscope (SEM)

Case Study – New Madrid Unit 2 – CaO Experience

Associated Electric Cooperative Inc. (AECI) contracted a joint venture of Black & Veatch and J.S. Alberici (BVCI/JSA) to provide a High Dust Selective Catalytic Reduction (SCR) system for their 640 MW New Madrid cyclone fired Units 1 & 2. Subsequently, BVCI/JSA subcontracted for catalyst supply from Cormetech. The project constituted the world's first application of SCR to a 100% PRB coal fired boiler. In addition to the unique characteristics of the fuel the project also required high NOx removal efficiency (93%) while maintaining low ammonia slip (3 ppmvdc).

The PRB fuel presented unique ash characteristics which influenced both pitch selection and catalyst deactivation. Its use in cyclone fired boilers results in chemical ash characteristics that are within the experience base, however use on pulverized coal fired units will present new challenges. The resulting mechanical characteristics of the ash lead to the selection of larger catalyst pitches.

Unit Description & Design Data

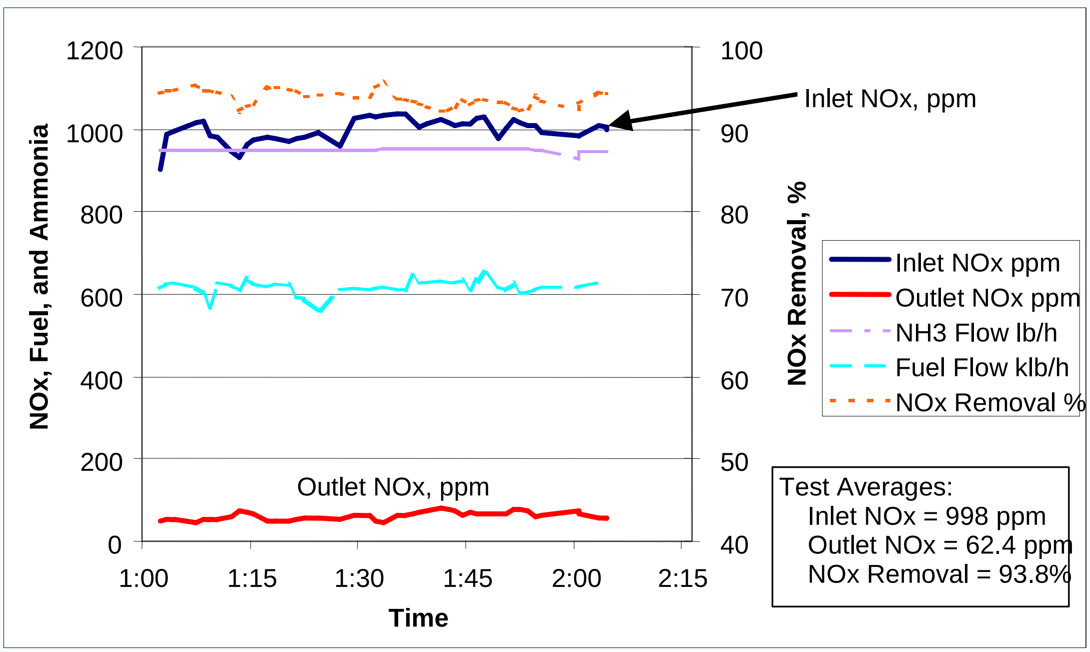
Boiler Type	B&W Cyclone Fired	
Start of Operation	Unit 1 – 1972 Unit 2 – 1977	
Number/Arrangement of cyclones	14 cyclones, opposed wall	
Heat Input, MMBtu/Hr (full load)	6,234	
Air Heater Type	Ljungstrom (new)	
Baseline NOx, lb/MMBtu	1.5	
Particulate Control	Cold Side ESP	
Ash Recirculation	None	
Fuel, Powder River Basin Coal		
Ultimate Analysis (%, dry basis)	Typical	Range
Carbon	69.2	64.5 – 74.5
Hydrogen	4.7	3.6 – 6.1
Nitrogen	0.9	0.6 – 1.3
Chlorine	0.03	0.01 – 0.15
Sulfur	0.3	0.2 – 0.8
Ash	6.2	5.3 – 9.8
Oxygen	18.7	16.0 – 21.0
Ash Analysis (%, Ignited Basis)	**Typical**	**Range**
P_2O_5	1.2	0.6 – 2.6
SiO_2	33.4	28.5 – 38.5
Fe_2O_3	5.2	3.6 – 7.5
Al_2O_3	16.3	14.2 – 20.2
TiO_2	1.2	0.5 – 1.6
CaO	**21.5**	**18.0 – 26.3**
MgO	6.4	4.7 – 8.7
SO_3	11.7	1.8 – 11.7
K_2O	0.35	0.2 – 0.8
Na_2O	1.9	0.9 – 2.7
BaO	0.6	0.2 – 0.9
SrO	0.27	0.01 – 0.50
MnO_2	0.02	0.02 – 0.20
Unburned Carbon	18	

Trace Element Analysis (ppm in coal dry basis)	Design
Silver	0.24
Arsenic	1.5
Boron	43
Barium	N/A
Beryllium	0.4
Bromine	N/A
Manganese	9.0
Nickel	5.0
Lead	5.0
Antimony	0.62
Selenium	0.3
Strontium	156.4
Cadmium	0.56
Cobalt	N/A
Chromium	6.0
Copper	12.0
Germanium	N/A
Mercury	0.10
Thallium	N/A
Uranium	N/A
Design Conditions, Full Load	
Flue gas mass flow rate, lb/hr	6,217,000
Flue gas temperature, ^oF	715 - 800
Particulate Concentration, gr/dscf	1.0
H_2O, vol %	14.9
O_2, vol %, dry	1.85
SO_2, ppmvd	170
SO_3, ppmvd	6.0
Catalyst Pitch, mm	9.2
Catalyst SO_2 conversion, %	3
Catalyst design life, hours	20,000

Table 3: New Madrid Unit 2 Coal Data

Selection of the most appropriate catalyst pitch is important to assure that ash will not deposit and bridge over the catalyst cells/openings, thus reducing the effective catalyst surface area and causing increased pressure loss. The properties of the ash generated by the New Madrid units were evaluated under various conditions and with multiple catalyst pitch selections. Catalyst selections included multiple pitches and open areas. Ultimately, after studying the options carefully and taking into consideration the properties of the ash, a 9.2 mm pitch product with a geometric surface area of 383 m^2/m^3 and an open area of 79.8% was chosen.

Chemical deposits/reactions on or within the catalyst are the primary cause for loss of NOx removal performance over time. The primary focus of catalyst performance degradation associated with the New Madrid units was attributed to the deposition and conversion of CaO to $CaSO_4$ within the catalyst pore structure. Deactivation caused by arsenic, and components such as sodium, potassium, and phosphorous are relatively small in comparison to $CaSO_4$. The deposition rate of CaO onto/into the catalyst surface is a function of the mass transfer rate within the catalyst cells. It is important to note that the deterioration caused by $CaSO_4$ is primarily dependent on the CaO content because it is the rate limiting step of the reaction. Therefore the content of SO_3 in the flue gas has a very limited affect on deterioration caused by this mechanism.



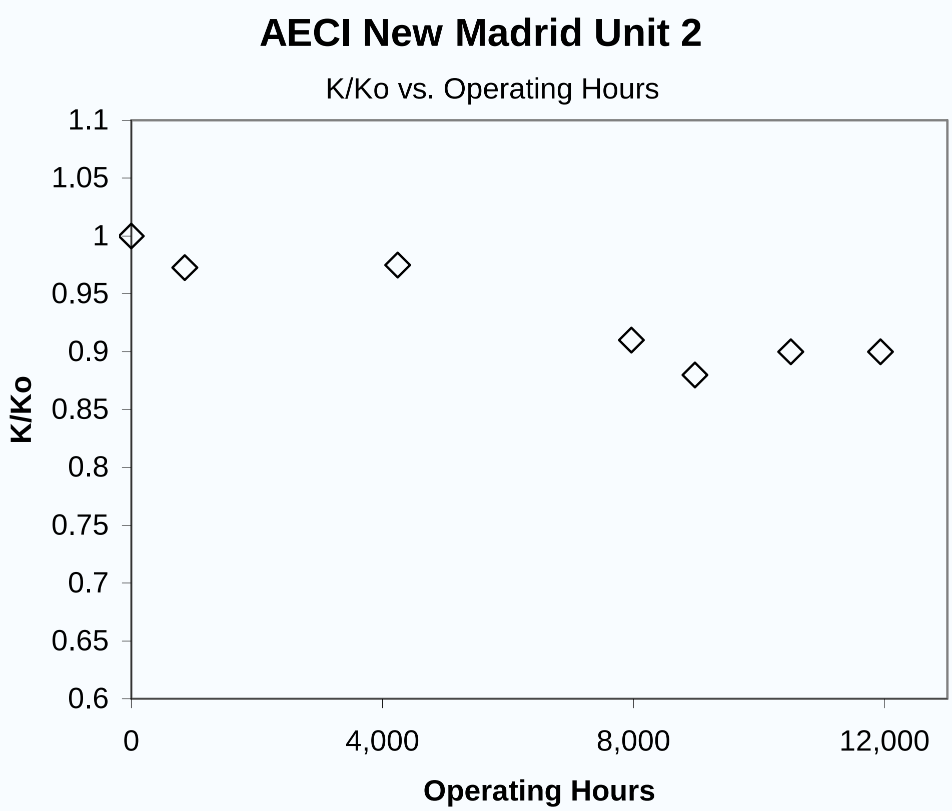
Graph 1: New Madrid Unit 2 audit test 2 (4,242 hours)

Catalyst samples were removed from the reactor at the following intervals and tested.

	Time On-Line (Hours)	**K/Ko**
Fresh Reference	0	1.00
First 2000 Audit	850	0.97
Second 2000 Audit	4,242	0.98
First 2001 Audit	7,966	0.91
Second 2001 Audit	8,975	0.88
Third 2001 Audit	10,503	0.90
First 2003 Audit	11,930	0.90

Table 4: AECI New Madrid Testing

This audit of the AECI New Madrid Unit 2 SCR catalyst shows a decrease in catalytic potential of the SCR catalyst, as measured by pilot-scale testing.



Graph 2: New Madrid Unit 2 Activity test results

Ash Build-Up and Catalyst Plugging

Understanding fly ash characteristics and evaluating plugging effects are an important tool in designing an SCR catalyst to meet performance requirments. Evaluation of the appropriate design includes not only the proper selection of catalyst pitch, but also the minimization of large particle ash (larger than 4 mm) carryover through proper hopper and equipment design and proper inlet flue design including vanes and structural supports. Physically, proper catalyst support beam design and an installation of wire mesh above the catalyst to capture or break down large particles is also a factor.

The mechanism of ash accumulation can be defined as the generation of coarse ash after combustion that is entrained in the gas stream leading to the catalyst and deposition of fine ash at static flow regions upstream of the SCR reactor where cohesion of fine ash forms agglomerates that release and fall on the catalyst surface causing bridge plugging. Ash accumulation can be evaluated by the Angle of Repose which can be considered a function of SO_3, Partical Size Distribution, Unburned HydroCarbon, Ph, CaO, Na, K surface chemistry and surface friction.

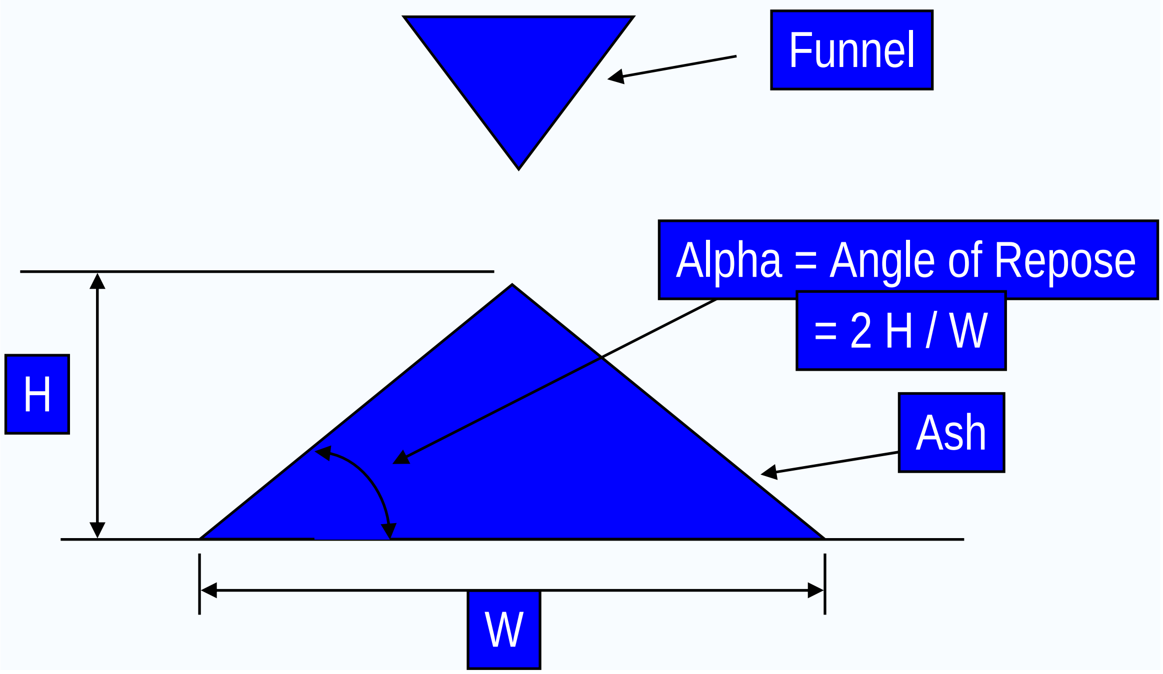


Figure 1: Angle of Repose

To confirm the tendency of ash plugging on various types of catalyst including rectangular pitch and plate catalyst, an ash plugging test was conducted by Mitsubishi Heavy Industries (MHI). The types of catalyst tested were:

	Open Area	Type
3 x 26 Catalyst	80%	Plate
16 x 16 Catalyst	79%	Honeycomb
21 x 21 Catalyst*	73%	Honeycomb

Table 3: Catalyst types tested for ash plugging

* Cormetech's current product that has replaced the 21 x 21 catalyst has an open area of 80%

In order to increase ash viscosity, flour was added to the ash sample.

Ash	Flour	Angle of Repose
0%	100 %	68° (at Room Temperature)
28%	72 %	52° (at Room Temperature)

Table 4: Angle of Repose – Ash viscosity

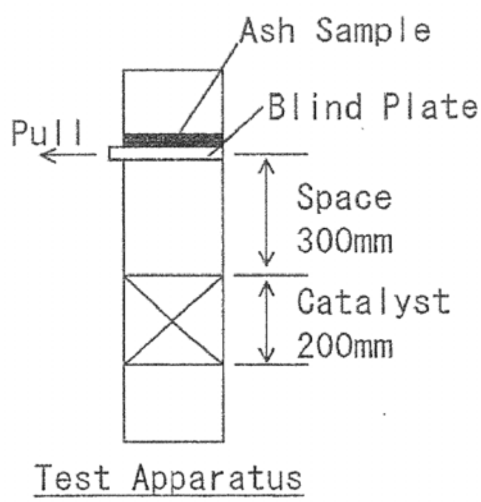


Figure 2: Test apparatus for Angle of Repose ash plugging test

Catalyst Model	Open Area	Type	0% Ash / 100% Flour 150 grams
3 x 26 Catalyst	80% open area	Plate	~21% Plugged
16 x 16 Catalyst	79% open area	Honeycomb	~6% Plugged
21 x 21 Catalyst	73% open area	Honeycomb	~10% Plugged

Table 5: Test Results for Ash Plugging (0% Ash / 100% Flour)

Catalyst Model	Open Area	Type	28% Ash / 75% Flour 250 grams
3 x 26 Catalyst	80% open area	Plate	~12% Plugged
16 x 16 Catalyst	79% open area	Honeycomb	~1% Plugged
21 x 21 Catalyst	73% open area	Honeycomb	~18% Plugged

Table 5: Test Results for Ash Plugging (28% Ash / 75% Flour)

The ash plugging test revealed that plate catalyst is just as likely to have plugging occur due to high ash loading as is the case with honeycomb catalyst. (Plugging has occurred in plate catalyst units throughout the United States on par with honeycomb units.) Catalyst type, either plate or honeycomb is just one factor that may impact plugging potential. The key to the prevention of ash plugging is to recognize ash characteristics and properties and also the elimination of large particle ash (LPA) which is particles greater than 4mm in any dimension.

Conclusion

China is at the beginning of a journey into a complex and new technology for the reduction of NO_x emissions. The understanding of the components that preclude the efficient and effective utilization of this new technology are easily misinterpreted and misconstrued. In order for an SCR catalyst design to meet the required criteria, plant and reactor conditions as well as design specifications must be accurate and understood. The CaO content and ash loading characteristics are an integral part of designing an SCR catalyst especially due to the coal types in China.

Cormetech not only has the capability to offer reliable SCR catalyst designs and guarantees for applications firing high calcium-bearing coals, Cormetech has a proven technology and the most extensive worldwide experience base in regard to high CaO content coal. With the largest installed base of successfully operating SCR units on high CaO applications, Cormetech has successfully replaced ineffective plate-type catalyst and has demonstrated fully operational applications that meet or exceed performance requirements.