

**PROCESO DE REVISIÓN REGULACIÓN EMISIONES EN CENTRALES
TERMOELÉCTRICAS DS-13 MINISTERIO DE MEDIOAMBIENTE DE
CHILE**

PROPUESTA SOLVAY

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REVISIÓN NORMA DE EMISIONES PARA CENTRALES TÉRMICAS DS-13

1. PRESENTACIÓN

SOLVAY, compañía química con más de 150 años de historia y presencia a nivel mundial, hace 30 años desarrolló una tecnología de abatimiento en seco (DSI, Dry Sorbent Injection por sus siglas en inglés), de gases ácidos, tales como HCl, SO_x, HF, Hg entre otros, basada en sorbentes de base sódica. Si bien la tecnología es apta para todo tipo de industrias, nuestra experiencia radica principalmente en el control de emisiones gaseosas de:

- Centrales termoeléctricas (independiente del tipo de combustible),
- Incineradoras de residuos urbanos y peligrosos con valorización energética (prácticamente todas las centrales europeas y otras partes del mundo han adoptado nuestra tecnología),
- Fábricas de vidrio para botellas y plano,
- Fábricas de cemento,
- Refinerías de petróleo,
- Siderúrgicas y producción de coque metalúrgico,
- Fundiciones de metales no ferrosos (entre ellas cobre), y purificación de minerales metálicos, Calderas industriales,
- Fábricas de papel,
- Control de emisiones en buques cargueros, pasajeros, ferris,

2. ACLARACIÓN

Es menester aclarar que nuestra experiencia radica en el abatimiento de gases ácidos (SO_x, HCl), y mercurio no así con respecto a NO_x, CO, CO₂ y metales pesados.

3. INTRODUCCIÓN

En el marco del actual llamado del Ministerio de Medioambiente, publicado en el Diario Oficial de la República de Chile: **“DA INICIO A LA REVISIÓN DE LA NORMA DE EMISIÓN PARA CENTRALES TERMOELÉCTRICAS, ESTABLECIDA MEDIANTE DECRETO SUPREMO N°13, DE 2011, DEL MINISTERIO DEL MEDIO AMBIENTE”**, SOLVAY Chile pone a disposición de dicho Ministerio toda su experiencia técnica tanto en el ámbito del tratamiento y mitigación de efluentes gaseosos como así también en la elaboración y revisión de normativas de emisiones como consultores permanentes en EEUU, Comunidad Europea y Asia, entre otros. Como expertos en el abatimiento de gases contaminantes desde hace ya más de 30 años, comprendemos detalladamente la problemática del impacto ambiental de los mismos y la necesidad de minimizar al máximo posible su emisión.

A lo largo de nuestra historia hemos sido partícipes activos de este proceso de aprendizaje y hemos logrado desarrollar una tecnología de abatimiento y control de gases contaminantes a la vez altamente eficiente y económicamente muy accesible en cuanto a sus costos de implementación y posterior operación sin perjuicio tanto para los operadores como para los activos.

En Chile venimos observando un proceso similar acaecido en otras partes del globo debido fundamentalmente a las siguientes razones no mensurables pero de gran peso;

1. Que según lo dispone el Decreto 13 publicado el 23 de Junio de 2011, donde indica que en la Constitución Política de la República se reconoce el derecho a la vida y la integridad física de las personas, además de "el derecho a vivir en un medio ambiente libre de contaminación", por tanto las regulaciones vigentes que datan del año 2011, resultan hoy insuficientes para el "nuevo" ciudadano Chileno que ya no tolera ni acepta más daños al medio ambiente.
2. Que una sociedad en evolución permanente requiere de mejora continua, por tanto, mejores y más estrictas regulaciones permitirán administrar cambios en beneficio de la salud de las personas.
3. Que disminuir los niveles de contaminantes, producen significativos ahorros a la Salud Pública, y al mismo tiempo pone al Estado en una mejor posición tanto en el manejo de la política interior como la exterior.
4. Que para todos los efectos, el MMA definió en su Decreto N°13, realizar revisiones a la ley cada cinco años con el objeto de hacer ajustes para mejorar la calidad del aire.
5. Reducir las emisiones, es alcanzable sin que ello implique dejar de lado las grandes inversiones que se realizaron en los últimos años, por el contrario son parte del proceso de mejoras medioambientales que ha sido parte de la política del MMA en los últimos 30 años.
6. Con relación a la última reunión COP25 realizada en Diciembre pasado en Madrid, la estrategia presentada por Chile lamentablemente no fue clara y dejó la impresión de que no se respetaba el acuerdo de París. Este motivo es de gran peso ante la comunidad internacional con la que Chile ha acordado compromisos y recuperar la credibilidad deslucida durante la COP25 sancionando límites de emisión más restrictivos.
7. Finalmente, el costo social impactado por las emisiones de fuentes fijas como las termoeléctricas como otras fuentes, se traduce en miles de dólares/euros por tonelada de contaminante emitido. Así por ejemplo en Europa alrededor del 1% de la población muere prematuramente por causas directamente relacionadas con los efectos de la contaminación. En el siguiente link se puede acceder a un informe del costo socio-económico de la contaminación en Europa: http://www.euro.who.int/_data/assets/pdf_file/0004/276772/Economic-cost-health-impact-air-pollution-en.pdf

Por otra parte, la experiencia de la EPA en EE.UU. en este sentido ha estimado los beneficios asociados con la reducción de la exposición a los tóxicos del aire. Cumplir con estos estándares reduce las emisiones de SO₂ y partículas finas (PM2.5) en aire. Esto mejoro significativamente la salud pública al prevenir cientos de miles de enfermedades y miles de muertes prematuras cada año. En 2016, la regulación evitó:

- ◆ 4.200 to 11.000 muertes prematuras,
- ◆ 2.800 casos de bronquitis crónica,
- ◆ 4.700 ataques cardíacos,
- ◆ 130.000 casos de asma agravada,
- ◆ 5.700 visitas a hospitales,
- ◆ 6.300 casos de bronquitis aguda,
- ◆ 140.000 casos de síntomas respiratorios,
- ◆ 540.000 días de trabajo perdidos,
- ◆ 3,2 millones de días en que las personas deben restringir su actividades por la polución,

La EPA estimo que los beneficios para la salud asociados con el cumplimiento de los estándar van de U\$D 37 mil millones a 90 mil millones en 2016.

Claramente entendemos y promovemos que el estado de las tecnologías actuales a la fecha provee una solución eficiente para lograr niveles de abatimiento nunca antes logrado a costos razonables, siendo el límite cero emisiones (o al menos lo que se entiende como fuera de la escala de medición de los instrumentos). En definitiva, hoy por hoy no cabrían excusas para no ajustar los límites de emisión a niveles más estrictos sin perjuicio alguno hacia la actividad económica de las fuentes emisoras.

Por lo anteriormente expuesto, en los párrafos sucesivos de esta presentación, intentaremos exponer las razones técnicas que justifiquen los límites de emisión que consideramos apropiados para la regulación de las termoeléctricas en Chile durante los próximos cinco años.

4. ABREVIATURAS

BACT: Best Available Control Technology (IE-EU)

Bicarbonato de sodio: NaHCO_3

BREF: Reference Documents (IE-EU)

CAPP: Central Appalachian Basin (Coal Source in Appalachian Mountains – USA)

CASPARR: Cross-State Air Pollution Rule (CSAPR) is a ruling by the United States Environmental Protection Agency (EPA) that requires member states of the United States to reduce power plant emissions that contribute to ozone and/or fine particle pollution in other states.

CEMS: Continuous Emission Monitoring System

DS-13: Decreto Supremo Número 13

DSI: Dry Sorbent Injection

EERC: Energy and Environmental Research Center (University of North Dakota – EE.UU.)

ESP: Electrostatic Precipitator

EPA: Environmental Protection Agency – EE.UU.

FF: Fabric Filter

FGD: Flue Gas Desulfurization

IED: Industrial Emission Directive

LCP: Large Combustions Plants (IE-EU)

MACT: Maximum Achievable Control Technology (EPA for boilers)

MATS: Mercury and Air Toxics Standards (EPA-USA)

MW_t: Mega Watts Térmicos (basados en el aporte energético del combustible)

NSR_T: Total Normalized Stoichiometric Ratio (sorbente/contaminante ingresante al tratamiento: SO_2 , HCl).

PTC: Particulate Test Combustor

SBC: Bicarbonato de Sodio

SOLVAir®: Marca registrada de Bicarbonato de sodio y Trona SOLVAY

TRONA: Sesquicarbonato de sodio ($\text{Na}_2\text{CO}_3 + \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$)

S200, S250: Marcas registradas de trona SOLVAY

S350, S450: Marcas registradas de Bicarbonato de sodio SOLVAY

SO_x: Dióxidos y trióxidos de azufre (SO_2 , SO_3)

HCl: Ácido clorhídrico

HF: Ácido fluorhídrico

NO_x: Dióxidos y monóxidos de nitrógeno (NO_2 , NO)

CO: Monóxido de carbono

CO₂: Dióxido de carbono

O₂: Oxígeno

H₂O: Agua (como humedad en gases)

Hg: Mercurio

5. LÍMITES DE EMISIÓN PROPUESTOS POR SOLVAY

Nuestra experiencia en termoeléctricas con base en combustibles sólidos como líquidos tanto en Europa, Estados Unidos, China, India y Chile avalan y justifica la disminución de los actuales límites de emisión para este importante sector industrial, establecidos en el actual DS-13. En su momento se estableció una diferencia entre fuentes viejas y nuevas, considerando como referencia temporal el 2011 como año de entrada en vigor de dicho decreto,

COMBUSTIBLE	MP [mg/Nm ³]	SO _x [mg/Nm ³]	NO _x [mg/Nm ³]
SÓLIDO	50	400	500
LÍQUIDO	50	30	200
GASEOSO	n.a.	n.a.	50

Tabla 1 – Límites emisión centrales antiguas.

COMBUSTIBLE	MP [mg/Nm ³]	SO _x [mg/Nm ³]	NO _x [mg/Nm ³]
SÓLIDO	30	200	200
LÍQUIDO	30	100	120
GASEOSO	n.a.	n.a.	50

Tabla 2 – Límites emisión centrales nuevas.

COMBUSTIBLE	Hg [mg/Nm ³]
Carbón/Petcoke	0,1

Tabla 3 – Límite emisión ambos tipos de centrales.

Entendiéndose como condiciones normales (N): 25 °C, 1 at.

A su vez, los límites de las tablas 1, 2 y 3 deben ser corregidos por O₂ en base seca, así:

- Calderas para generación de vapor: 6% O₂ para combustibles sólidos y 3% O₂ para combustibles líquidos y gaseosos.
- Turbinas que combustionan combustibles líquidos o gaseosos: 15% O₂.
- Ciclos combinados, turbinas y caldera: 15% O₂.

De acuerdo a nuestro criterio, los nuevos límites de emisión no deberían contemplar una división temporal con relación a las centrales: antiguas y nuevas. De aquí en más se debería considerar un único nivel de emisiones, respetando las consideraciones del presente decreto establecidas en 2011:

- Tipo de combustible: Sólido, líquido, gaseoso.
- Tipo de central: Caldera, turbina, ciclo combinado.
- Exenciones: Como la establecida en el Artículo 13 del presente decreto para fuentes emisoras entre 50 y 150 MWt).

Siendo entonces nuestra propuesta la siguiente:

COMBUSTIBLE	SO _x * [mg/Nm ³]**	HCl [mg/Nm ³]**	Hg [mg/Nm ³]**
SÓLIDO	130	5	0,1
LÍQUIDO	100	5	--
GASEOSO	--	--	--

Tabla 4 – Límites de emisión propuestos por SOLVAY.

*El límite para SO_x, expresado como SO₂ incluye SO₃ medible dos veces al año.

**Condiciones Normales a 25 °C, 1 at, 6% O₂ y seco.

Se consideran las mismas condiciones de medición en chimenea a través de los sistemas de monitoreo continuo CEMS, ya establecidos en el presente decreto.

Cómo se puede observar, sugerimos incluir el monitoreo de las emisiones de HCl por estar presente como cloruros en los carbones que actualmente se combustión en Chile, y que durante la combustión se transforman en dicho gas ácido. El mismo es responsable de la corrosión ácida encubierta en los sistemas de abatimiento de gases, polvos y hasta en chimenea, además de ser altamente nocivo para la salud humana.

6. JUSTIFICACIÓN DE LOS LÍMITES PROPUESTOS POR SOLVAY

Con el objeto de brindar razones probadas que justifiquen los límites de emisión que proponemos, a continuación describimos nuestra experiencia práctica en centrales térmicas donde damos pruebas de la capacidad de abatimiento de la tecnología de inyección de sorbentes en seco tanto para SO₂ como para HCl; así como también un preclaro estudio realizado en conjunto con el EERC de la Universidad de Dakota del Norte. También describimos nuestra larga relación con la autoridad ambiental europea como consultores permanentes.

1. Planta generadora con base combustible sólido (Chile) – Captación de SO₂
2. Planta generadora con base combustible sólido (Estados Unidos) – Captación de HCl
3. Estudio realizado en conjunto con el EERC Universidad de Dakota del Norte
4. Descripción de los Límites de Emisión para LCP Europa
5. Actividad Relacionada con Autoridad Ambiental Europea
6. Conclusiones

Nota: Es menester aclarar que por compromiso de confidencialidad acordado con nuestros clientes no nos es permitido revelar su nombre.

6.1. PLANTA GENERADORA CON BASE COMBUSTIBLE SÓLIDO (CHILE) – CAPTACIÓN DE SO₂

En esta descripción se demuestra la capacidad de los sorbentes sólidos secos de base sódica con respecto a elevados niveles de abatimiento de SO₂.

Se realizó ensayo con sorbente sódico SOLVAir S350 (Bicarbonato de sodio), en planta generadora de energía de base carbón, situada en Chile, entre el 18 y el 20 de Junio de 2016. La línea de proceso sigue la disposición típica de una termoeléctrica de base carbón mineral. Esta compañía seleccionó en su momento como sistema de control de emisiones la inyección de sorbentes en seco DSI; siendo las características operacionales de la unidad al momento del ensayo:

CARACTERÍSTICA	VALOR
Potencia bruta de base [MW]	150
Concentración inicial SO ₂ [mg/Nm ³]	820
Temperatura gases ingreso FF [°C]	160

Tabla 5 – Características operacionales termoeléctrica.

El carbón utilizado fue de tipo lignítico, siendo sus características y composición elemental las siguientes:

CARACTERÍSTICA	VALOR (c/recibido)
L.H.V [Kcal/kg]	6.214
Carbón [% w/w]	64,74
Hidrógeno [% w/w]	4,57
Oxígeno [% w/w]	9,51
Nitrógeno [% w/w]	1,17
Azufre [% w/w]	0,52
Cenizas [% w/w]	8,84
Agua [% w/w]	10,62

Tabla 6 – Características carbón.

A continuación se presenta el comportamiento del abatimiento del SO₂ durante el ensayo:

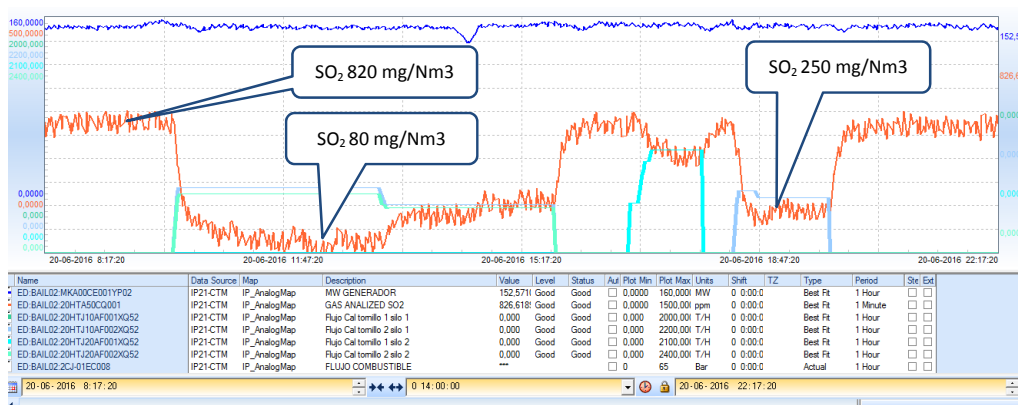


Gráfico 1 – Dosificación SOLVAir

Como se puede observar, se lograron niveles de abatimiento inferiores a 100 mg/Nm³.

6.2. PLANTA GENERADORA CON BASE COMBUSTIBLE SÓLIDO (USA) – CAPTACIÓN DE HCl

Sigue a continuación un interesante ejemplo para demostrar la capacidad de los sorbentes de base sódica en cuanto al abatimiento de HCl.

El presente ensayo se realizó en una termoeléctrica de base carbón mineral situada sobre el río Potomac, en el área de Washington, D.C.. Se trata de cinco unidades con un total de 482 MW. Se realizaron ensayos en la unidad 1 de 88 MW de capacidad neta, durante el 2005, utilizándose sorbentes de base sódica, Trona y Bicarbonato de Sodio.

Se condujeron **32 ensayos** a diferentes cargas de la unidad y con un carbón de la cuenca de los Apalaches centrales. En todos los ensayos se logró un abatimiento del 80% del SO₂ y mayor al 96% del HCl ingresantes, respectivamente.

La opacidad de los gases en chimenea se controló durante todo el período de ensayos, permaneciendo constante en un 4%, indicando ningún tipo de alteración en el nivel exigido de MP en chimenea.

El carbón utilizado corresponde a la cuenca de los Apalaches Centrales, siendo sus características y composición elemental las siguientes:

CARACTERÍSTICA	VALOR (c/recibido)
L.H.V [Kcal/kg]	6.387
Carbón [% w/w]	71,63
Hidrógeno [% w/w]	5,04
Oxígeno [% w/w]	10,05
Nitrógeno [% w/w]	1,22
Azufre [% w/w]	0,78
Cenizas [% w/w]	11,28
Cloruros [% w/w]	0,096

Tabla 7 – Carbón de los Apalaches Centrales.

En la siguiente gráfica se puede observar el rendimiento de Trona y Bicarbonato de Sodio (SBC),

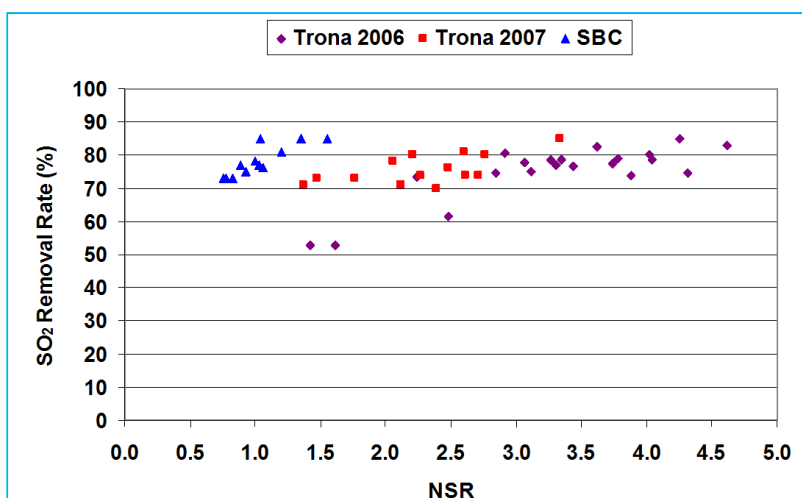


Gráfico 2 – Curvas rendimiento sorbentes sódicos. Termoeléctrica EE.UU.

Si bien ambos sorbentes logran elevados niveles de abatimiento de SO₂ claramente se observa una mayor reactividad de Bicarbonato de Sodio frente a Trona y con un menor consumo. Con relación al efecto sobre el desempeño del ESP, no se observaron desviaciones.

El abatimiento de SO₂ resultó en un 96% para Bicarbonato de Sodio y en un 99% para Trona.

6.2.1. ABATIMIENTO DE HCl

Tanto para Trona como Bicarbonato de Sodio logran emisiones de HCl muy por debajo de los límites de emisión para estos gases.

	Trona Injection	SBC Injection	Permit Limit
HCl	0,0011 lb/MMBTU 1,17 mg/Nm ³	0,0027 lb/MMBTU 2,86 mg/Nm ³	0,0072 lb/MMBTU 7,64 mg/Nm ³

Tabla 8 – Nivel abatimiento HCl con sorbentes sódicos.

6.3. ESTUDIO REALIZADO EN CONJUNTO CON EL EERC UNIVERSIDAD DE DAKOTA DEL NORTE

Dado que la tecnología SOLVAir® para abatimiento de gases ácidos en seco es prácticamente empírica, con el presente estudio se buscó un aval a nivel de laboratorio y lograr una comprensión más acabada de los complicados procesos de transporte de masa y energía que se suscitan en las reacciones sólido – gas.

SOLVAY contrató al Centro de Investigación de Energía y Medio Ambiente (EERC), de la Universidad de Dakota del Norte, para realizar una prueba de combustión a escala piloto de manera tal evaluar el rendimiento de abatimiento de gases ácidos de los sorbentes SOLVAY: Trona (S200, S250), SOLVAir (S350 y S450). Se seleccionó un carbón de los Apalaches centrales (CAPP), como carbón de prueba.

Los objetivos de eliminación de HCl se establecieron en 80%, 90% y 99% para cada sorbente para determinar las tasas de alimentación reales sobre la marcha. Para fines de comparación, la cal hidratada también se probó para la eliminación de gases ácidos en un FF en las mismas condiciones de gases de combustión.

Para las pruebas con ESP, cada sorbente redujo las emisiones de HCl por debajo de los límites propuestos por la tecnología de control máximo alcanzable de la EPA (MACT), comprobándose así que la tecnología existente puede controlar la emisión de HCl sin limitaciones.

Encontrar en **Anexo 1** el estudio realizado con el EERC.

Si bien durante el presente ensayo se pretendió simular lo mejor posible las condiciones reales del proceso de abatimiento de gases que se presentan a escala industrial en una termoeléctrica de base carbón, no deja de ser un ensayo a escala de laboratorio con sus limitaciones inherentes.

6.4. DESCRIPCIÓN DE LOS LÍMITES DE EMISIÓN PARA LCP EUROPA

En **Anexo 2** se adjunta tablas con diferentes límites de emisión establecidos por BATC EU para las plantas termoeléctricas de elevada potencia (LCP, Large Combustion Plants). Los límites de emisión se definieron en función de la potencia térmica generada, el tipo de combustible: Sólido, líquido, gaseoso e inclusive biomasa.

La biomasa se define como "**la fracción biodegradable de productos, desechos y residuos de origen biológico de la agricultura (incluidas las sustancias vegetales y animales), la silvicultura y sus industrias relacionadas, incluida la pesca y la acuicultura, así como la fracción biodegradable de los desechos industriales y municipales**" (fuente : Directiva sobre energías renovables, EU).

La necesidad de poner límites a las emisiones en la combustión de biomasa está vinculada a cuestiones ecológicas y económicas para su comprensión en la UE. Así, por ejemplo, **los mayores emisores de dioxinas** son las fuentes fijas que **combustionan biomasa** como es el caso de la madera utilizada como combustible. Por tanto sugerimos contemplar la inclusión de este combustible en la presente revisión del DS-13, de manera tal que esta (combustión de biomasa), cumpla con los nuevos límites que surjan de la revisión.

Tener presente que en Chile existen más de 500 MW de energía generada a partir de biomasa (link: <http://generadoras.cl/tipos-energia/bioenergia>).

6.5. ACTIVIDAD RELACIONADA CON LA AUTORIDAD AMBIENTAL EUROPEA

A continuación se describe la experiencia de colaboración de SOLVAY con la autoridad Europea **JRC EIPPCB (Joint Research Center European Integrated Pollution Prevention and Control Bureau)**, durante los últimos 10 años, participando en la revisión de las **BREF/BATC**,

- **CWW** (Common Waste water Waste gas)
- **WT** (Waste treatment Bref working on the residual from flue gas treatments)
- **LCP** (Large combustion plant) regarding all combustion plant > 50 thermal MW without differentiation on the use of the produce heat (In the revision we can suggest to merge the industrial boiler legislation with this one).
- **WI** (waste incineration)
- **WGC** (Waste gas in Chemical plants)

Cooperación con **EU General Direction "Calidad de Vida"**, ambición de contaminación cero, guías respecto al modo de alcanzar valores de emisión cercanos a cero en fuentes industriales fijas.

Cooperación con **EU General Direction "Environment" IED (Industrial Emission Directive)**, revisión de la evaluación inicial de impacto ambiental.

Cooperación con **OECD (Organization for Economic Co-operation and Development, United Nation agency in charge of development)**.
OECD BAT extension project.

7. CONCLUSIONES

- Nuestra experiencia en termoeléctricas y los distintos ensayos que hemos realizado, demuestran que es posible lograr fácilmente niveles de emisión por debajo de los 100 mg/Nm³ SO₂. Por tanto con base en estos resultados se puede sostener que con las distintas tecnologías existentes hoy en el mercado actual se podrían exigir límites de emisión más restrictivos.
- Los sorbentes de base sódica pueden lograr niveles de abatimiento de SO₂ superiores al 96% y de HCl del orden del 99%.
- Consideramos que el desafío de la actual revisión es establecer un límite que concilie el costo operativo de las compañías para cumplimentar con los límites de emisión establecidos en el DS-13 y los nuevos límites que se establezcan a partir de esta revisión. Por tal motivo y de acuerdo a nuestra experiencia, creemos que el equilibrio puede alcanzarse con un límite de 130 mg/Nm³ de SO₂.
- Creemos oportuno incluir en la presente revisión una limitación a la emisión de HCl, debido a que los carbones que se consumen presentan contenido de cloruros, como actualmente lo consideran las regulaciones Europea y Americana. El mismo es responsable de la corrosión ácida encubierta en los sistemas de abatimiento de gases, polvos y hasta en chimenea, además de ser altamente nocivo para la salud humana.
- Sugerimos contemplar la inclusión de biomasa como combustible en la presente revisión del DS-13, de manera tal que esta, cumpla con los nuevos límites, toda vez que la misma es un gran contribuyente a la emisión de HCl y dioxinas.
- En EE.UU. se estiman que los beneficios para la salud asociados con el cumplimiento de los estándares van de U\$D 37 mil millones a 90 mil millones en 2016.
- En la UE, la contaminación ambiental causa más de 1.000 muertes prematuras de media al día, más de diez veces el número de víctimas fatales por accidente de tráfico.

ANEXOS

ANEXO 1

Informe EERC Universidad de Dakota del Norte



EERC

Energy & Environmental Research Center

000172 vta

UNIVERSITY OF NORTH DAKOTA

15 North 23rd Street — Stop 9018 / Grand Forks, ND 58202-9018 / Phone: (701) 777-5000 Fax: 777-5181
Web Site: www.undeerc.org

February 22, 2012

Dr. Yougen Kong
Technical Development Manager
Solvay Chemicals, Inc.
3333 Richmond Avenue
Houston, TX 77098

Dear Dr. Kong:

Subject: Technical Report Entitled “Reduction of Acid Gases of HCl, SO₂, and NO_x Using Solvay Sorbent in Low-Sulfur Coal Flue Gases”; EERC Fund 17087

Please find attached the technical report. If you have any questions, please contact me by phone at (701) 777-5236, by fax at (701) 777-5181, or by e-mail at yzhuang@undeerc.org.

Sincerely,

Ye Zhuang
Research Manager

YZ/kal

Attachment



REDUCTION OF ACID GASES OF HCl, SO₂, AND NO_x USING SOLVAY SORBENT IN LOW-SULFUR COAL FLUE GASES

Technical Report

(for the period September 1, 2011, through February 29, 2012)

Prepared for:

Yougen Kong

Solvay Chemicals, Inc.
3333 Richmond Avenue
Houston, TX 77098

Prepared by:

Ye Zhuang

Energy & Environmental Research Center
University of North Dakota
15 North 23rd Street, Stop 9018
Grand Forks, ND 58202-9018

February 2012

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REDUCTION OF ACID GASES OF HCl, SO₂, AND NO_x USING SOLVAY SORBENT IN LOW-SULFUR COAL FLUE GASES

ABSTRACT

Solvay Chemicals, Inc., contracted the Energy & Environmental Research Center to perform a pilot-scale combustion test to evaluate the acid gas removal performance of Solvay sorbents S200, S250, S350, and S450. A Central Appalachian (CAPP) coal was selected as the test coal.

The sorbent injections were upstream of an electrostatic precipitator (ESP) at 650°F in one case and upstream of a fabric filter (FF) at 325°F in another case. The injection rates varied from 0.39 to 2.18 g/dNm³. HCl removal targets were set at 80%, 90%, and 99% for each sorbent to determine actual feed rates on the fly. For the purpose of comparison, hydrated lime was also tested for acid gas removal in a FF under the same flue gas conditions. One continuous HCl monitor was used at the ESP/FF outlet to monitor gaseous HCl emissions for each test condition. U.S. Environmental Protection Agency (EPA) Method 26 data were also collected for selected test conditions to verify the measurement by the continuous HCl analyzer. Under the ESP test, each sorbent reduced HCl emissions below the proposed EPA maximum achievable control technology (MACT) rules for HCl. For FF testing, only S250 met the removal requirement by the MACT rules for HCl. SO₂ was also removed during sorbent injection in both configurations; but none of the tested sorbents achieved the SO₂ limits proposed under MACT rule. NO_x appeared to be reduced more when sorbents were injected upstream of the ESP than when they were injected upstream of the FF.

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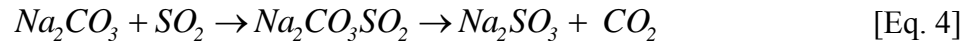
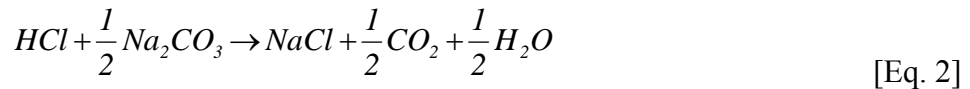
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REDUCTION OF ACID GASES OF HCl, SO₂, AND NO_x USING SOLVAY SORBENT IN LOW-SULFUR COAL FLUE GASES

INTRODUCTION

With the new maximum achievable control technology (MACT) rule on emissions of hazardous air pollutants (HAPs), the utility industry needs to determine its control strategies on HCl, SO₂, NO_x, particulate matter (PM), mercury, and other trace elements to meet regulatory requirements.

Sodium-based sorbent such as trona has been considered a cost-effective solution to acid gas reduction. Many bench-scale laboratory studies previously conducted have focused on SO₂ adsorption mechanisms. In real application, as dry sodium-based sorbent contacts flue gas, not only is SO₂ adsorbed by the sorbent, but also other acid gases such as HCl. The following chemical reactions take place to capture HCl and SO₂. Meanwhile, studies have shown that sodium-based sorbent can provide a partial reduction of NO_x as well.



Physical characteristics of injected sorbent, such as size and morphology, reaction temperature, reaction time, stoichiometric ratio (SR), and initial concentrations of acid gases (e.g., HCl and SO₂) in flue gas, are the major factors that affect capture efficiencies of individual acid gases. Bench-scale laboratory experiments were conducted to understand the effect of each individual parameter on acid gas adsorption. Sorbent size appeared to be the most important factor influencing the reaction of sodium sorbent with HCl and SO₂. Although the smaller the sorbent, the higher the acid gas capture efficiencies because of higher mass transfer rate and more surface area, the optimum sorbent size for acid gas removal in a full-scale application is determined not only by acid gas removal efficiency, but also by other factors such as cost and material-handling issues.

Contact time between sorbent and acid gas is mainly determined by the particulate control devices used. Dry sorbent injected in an electrostatic precipitator (ESP) application only contacts flue gas in flight for a few seconds, while sorbent attached to a fabric filter (FF) remains in the flue gas stream for many minutes. Although longer contact times, in theory, will result in higher acid gas adsorption, studies have shown that the sorbent surface may be plugged by the reaction products; therefore, sorbent utilization may decrease with time.

Temperature is another important factor affecting acid gas adsorption on sodium sorbent; however, its effect on acid gas capture is complicated. For example, higher temperature results in highly reactive sodium sorbent with faster reaction rates but may also cause sintering of the sorbent, subsequently reducing sorbent efficacy. Public data indicate no steady trend of capturing acid gases with sodium sorbent with a change in temperature, since temperature will affect acid gas adsorption by affecting other parameters.

Increasing the SR results in high-acid-gas capture efficiency, although sorbent utilization may not necessarily be optimum. Economic factors need to be considered if a high SR is applied.

Since there will be interactions between the flue gas species as well as competition between species to react with the sorbent, these parameters are coupled with each other. The corresponding overall impact on acid gas capture in full-scale injection is not straightforward. It is difficult to identify the optimum operating condition of sodium sorbent injection during full-scale demonstration, since there are many other uncontrolled and varying factors, such as coal type, plant load, and plant operating conditions, which impede drawing valid conclusions. Systematic study in a pilot-scale unit, which has representative flue gas characteristics such as those in a full-scale unit but with controlled operating conditions, is a desirable step to understand the overall effect of coupled parameters on sodium sorbent performance and determine and/or develop the optimum strategy of sodium injection.

PROJECT OBJECTIVE

The overall goal of this project is to characterize the performance of Solvay sorbent in capturing HCl, SO₂, and NO_x in low-sulfur coal flue gas. Specific objectives include the following:

- Quantify the effect of the size of Solvay sorbent on capturing HCl, SO₂, and NO_x in Central Appalachian (CAPP) coal flue gases with an ESP.
- Compare the performance of Solvay sorbent and hydrated lime on the capture of HCl, SO₂, and NO_x in CAPP coal flue gases with a FF.

EXPERIMENTAL DESCRIPTION

Pilot-Scale Combustion Facility

A pilot-scale pulverized coal combustor with an approximate firing output of 550,000-Btu/hr was used for the project. A schematic of the PTC is shown in Figure 1. The entire system is designed to generate flue gas and fly ash representative of that produced in a full-scale utility boiler. The time–temperature profile of the pilot unit is typical of that of a full-scale system. A suite of different air pollution control devices, including an ESP, a FF, selective catalytic reduction (SCR), and wet/dry scrubbers, are available for the system, while ESPs and FFs are of interest to Solvay and were used during the sorbent injection.

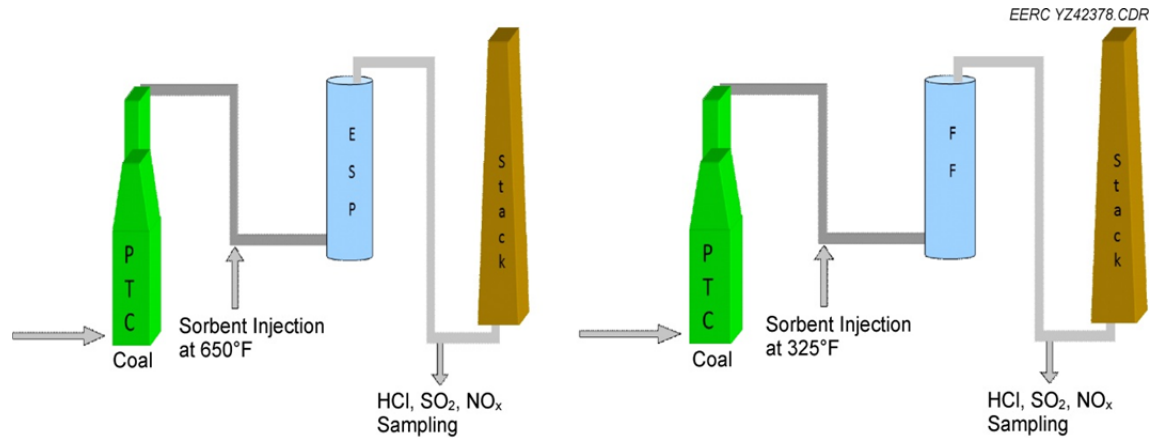


Figure 1. Schematic diagram of test configurations.

For all tests, the flue gas from the combustor routed through a series of heat exchangers followed by a particulate control device, which can be either an ESP or a FF. The single-wire tubular ESP was maintained at 325°F, and the actual flow rate of flue gas through the ESP was ~196 acfm, providing 2.4 seconds of residence time for the flue gas within the ESP. The FF vessel is a 20-in.-i.d. chamber and is equipped with three FF bags (new Ryton-type bags, 13 ft in length and 5 in. in diameter). The FF was operated at 325°F with a nominal 3.7-ft/min air-to-cloth ratio across the three FF during the test. Each bag is periodically cleaned separately with its own diaphragm pulse valve. Pressure drop across the FF was monitored during the injection tests.

Experimental Approach

A CAPP coal was chosen for the combustion tests performed in September 2011. The sorbents selected were milled (S250) and unmilled (S200) trona, milled (S450) and unmilled (S350) sodium bicarbonate, and commercially available hydrated lime. These sorbents were evaluated in the ESP and the FF configuration, respectively. Solvay indicated that the purity of the trona sorbent was 97.5% and 100% for the sodium bicarbonate. The purity of the hydrated lime used in the test was 96.8%. Table 1 summarizes sorbent details used for the test.

For the ESP configuration, The sorbent was injected into the flue gas upstream of the ESP where the temperature was 650°F. It was estimated that it would take 2.1 seconds for the injected

Table 1. Sorbent Information

Sorbent Type	Chemical Formula	Sorbent Size	Injection Temp., °F
Trona (S200)	$\text{Na}_3(\text{CO}_3)(\text{HCO}_3) \cdot 2(\text{H}_2\text{O})$	As received	650, 325
Trona (S250)	$\text{Na}_3(\text{CO}_3)(\text{HCO}_3) \cdot 2(\text{H}_2\text{O})$	d_{50} : 20 μm	650, 325
Sodium Bicarbonate (S350)	NaHCO_3	d_{90} : 40 μm	650, 325
Milled Sodium Bicarbonate (S450)	NaHCO_3	d_{90} : 20 μm	650
Hydrated Lime	$\text{Ca}(\text{OH})_2$	d_{90} : 45 μm	325

sorbent to reach the ESP. During the ESP testing, the ESP was cleaned out off-line between each sorbent change to recover baseline. For the FF testing, sorbents were injected at the inlet of the FF where the temperature was at 325°F. The FF bags were pulsed between each feed rate change as well as for each sorbent to recover baseline and minimize residual effect. A volumetrically controlled dual screw feeder was used for sorbent feed ESP testing, and a gravimetrically controlled feeder was used during the FF testing. The sorbent feeder change was done to provide higher accuracy for the low feed rates experienced during FF injection and to provide feedback on weight verification.

The unit started with an 8-hr heat-up period on gas and then with steady-state operation firing coal. Table 2 lists test conditions, sorbent feed rate, and sampling activities that were completed.

Coal combustion baseline condition was established for several hours, and U.S. Environmental Protection Agency (EPA) Method 26 (M26) measurement of HCl was taken during this baseline test to verify the continuous HCl analyzer measurement. The ESP ash was removed prior to the first sorbent injection.

The first sorbent injected at 650°F upstream of the ESP was S200. The feed rate was initially too high and was adjusted to obtain the first target of close to 80% removal. The feed rate was increased through two other feed rate points to achieve ~90% and ~99% HCl removal, respectively, as determined by the continuous HCl analyzer. The ESP was not cleaned out between each injection rate for a single sorbent but rather was cleaned of sorbent between sorbent changes. The second, third, and fourth sorbents injected upstream of the ESP were S250, S350, and S450, respectively. Each sorbent was injected at three rates in order to achieve the

Table 2. Completed Test Matrix and Sampling Activity

Test Series No.	Test Description	Sorbent Injection Rate, g/dNm ³	HCl Sampling Activity	Note:
T-0	Baseline, CAPP	0	HCl analyzer, 1-M26	Establish HCl baseline at ESP out
T-1	S200 sorbent injection upstream of ESP	1.08, 1.52, 2.77	HCl analyzer, 1-M26 at selected rate	Establish HCl removal trends, target 80%, 90%, and 99%
T-2	S250 sorbent injection upstream of ESP	0.87, 1.34, 1.75, 1.99	HCl analyzer, 1-M26 at selected rate	Establish HCl removal trends, target 80%, 90%, and 99%
T-3	S350 sorbent injection upstream of ESP	0.44, 0.87, 1.13	HCl analyzer, 1-M26 at selected rate	Establish HCl removal trends, target 80%, 90%, and 99%
T-4	S450 sorbent injection upstream of ESP	0.41, 0.55, 0.71	HCl analyzer	Establish HCl removal trends, target 80%, 90%, and 99%
T-5	S200 sorbent injection upstream of FF	0.72, 1.06, 1.69	HCl analyzer	Establish HCl removal trends, target 80%, 90%, and 99%
T-6	S250 sorbent injection upstream of FF	0.71, 0.8, 1.35	HCl analyzer	Establish HCl removal trends, target 80%, 90%, and 99%
T-7	S350 sorbent injection upstream of FF	0.39, 1.28, 1.83	HCl analyzer	Establish HCl removal trends, target 80%, 90%, and 99%
T-8	Hydrated lime injection upstream of FF	2.18	HCl analyzer	One comparison point for hydrated lime

target HCl removal rates (~80%, ~90%, and ~99%). Between each different sorbent injected, the ESP was taken off-line for cleaning. When the ESP was brought back online, the baseline HCl measurement was reestablished before the next sorbent injection.

After the ESP tests were completed, the pilot-scale system was switched from an ESP configuration to a FF configuration. In order to minimize any residual effect caused by the sorbent attached to the filter surface and maintain reasonable pressure drop across the filters, it was determined that each injection would be 40 minutes long to reach stable HCl emission and that the FF would be pulsed between each injection rate as well as for each sorbent to remove used sorbent.

Coal Data

Composite coal samples were collected during the course of testing by collecting a portion of the pulverized coal each time the coal feed hopper was refilled. The collected coal sample was then analyzed for proximate–ultimate and chlorine content. It should be noted that the moisture content for samples of the pulverized coal feed is on an as-fired basis since some drying of the coal occurs during coal preparation and pulverization at the EERC.

Flue Gas Sampling

Routine flue gas samples were taken and analyzed at two locations: the outlet of the combustor and the outlet of the PM control device (ESP or FF). After the flue gas passed through sample conditioners to remove the moisture, a pair of Rosemount Analytical NGA-2000 MLT3 multicomponent continuous gas analyzers were used for analysis of O₂, CO, and CO₂. NO_x is determined using a pair of Rosemount Analytical NO_x chemiluminescent analyzers. SO₂ was measured using a pair of Ametek Instruments photometric gas analyzers. Each of these analyzers was regularly calibrated and maintained to provide accurate flue gas concentration measurements.

Flue gas HCl concentrations at the outlet of the PM control device (ESP or FF) were measured using a HCl analyzer (Thermo 15C). The Model 15C utilizes a gas filter correlation nondispersive spectrometer to measure the specific HCl infrared absorption at 3.4 μm and has served as the primary instrument for HCl measurement in flue gas. The Model 15C was calibrated at both 5 and 90 ppmv on a daily basis. Meanwhile, measurement validation was performed using EPA M26 and compared with the estimated chlorine concentration in the flue gas based on chlorine content in coal.

Acid Gas Reduction Calculations

Acid gas reductions are calculated according to Equation 5, which uses the preinjection ESP/FF outlet acid gas concentration as the baseline value. Acid gas reductions calculated in this way then represent acid gas capture attributable solely to sorbent injection.

$$AcidGas\ Reduction_{AboveBaseline} = \frac{AcidGas_{Pr\ injection} - AcidGas_{DuringTest}}{AcidGas_{Pr\ injection}} \times 100\% \quad [Eq. 5]$$

Also, by referencing the pretest conditions, it was possible to compensate for the inherent coal variability. Averaged values of HCl, SO₂, and NO_x concentrations were computed and used for the acid gas reduction calculations. Complete plots of the acid gas test data are provided in Appendix A.

Total Stoichiometric Ratio Calculations

The injection rate of sorbent was converted to a total stoichiometric ratio (SR_T) for comparing performance of different sorbents. SR_T, as shown in Equation 6, is defined as dividing the actual sorbent injection rate by stoichiometric required sorbent to neutralize all SO₂ and HCl in flue gas.

$$SR_T = \frac{F}{\sum_i (X_i \cdot \beta_i)} \quad [\text{Eq. 6}]$$

Where F is the actual sorbent injection rate, g/hr; X_i is the actual acid gas flow rate in flue gas; β_i is the stoichiometric required sorbent to neutralize acid gas of X_i.

RESULTS/DISCUSSION

CAPP Coal Data and Flue Gas Composition

The analyses of the CAPP coal composite included proximate, ultimate, and chlorine content, and the results are list in Table 3. The average chlorine concentration of the tested coal is 962 ppm (average, dry basis). Based on the proximate and ultimate analysis data obtained and the chlorine content in the coal, a theoretical combustion calculation indicates that approximately 0.106 g/dNm³ of total HCl was expected in the gas stream at a 3% oxygen level. The continuous HCl monitor detected 0.10–0.121 g/dNm³ HCl (3% O₂) in the preinjection baseline flue gas, which is within 5.7%–14.2% of the theoretical value.

Baseline Data

Tables 4 and 5 present the typical flue gas composition measured at the combustor outlet with no sorbent injection for the ESP and FF tests, respectively. The particulate test combustor (PTC) is operated with an excess oxygen concentration of 4%–5% to ensure complete combustion with minimum unburned carbon leaving the combustor.

HCl measurement by the HCl analyzer at the ESP outlet under the baseline conditions was 80 ppmv (0.121 g/dNm³ at 3% O₂), which agrees well with the EPA M26 results of 77 ppmv (0.117 g/dNm³ at 3% O₂). HCl baseline concentration was ~75 ppmv for the FF tests.

Table 3. Summary of Coal Analyses for CAPP

Proximate Analysis, as received,%	Sample 1	Sample 2
Moisture	2.79	2.64
Volatile Matter	33.76	33.24
Fixed Carbon	52.16	52.26
Ash	11.29	11.85
Ultimate Analysis, as received, %		
Hydrogen	5.04	5.05
Carbon	71.63	72.63
Nitrogen	1.22	1.22
Sulfur	0.78	0.78
Oxygen (Ind)	10.05	8.48
Ash	11.28	11.85
Heat Value, Btu/lb	11,496	
Chlorine, µg/g	954–970	

**Table 4. Typical Flue Gas Composition
Baseline for ESP Tests at Combustor Outlet**

O ₂ , dry, vol % ^a	4.5
CO ₂ , dry, vol %	14.9
SO ₂ , dry, ppmv	565
NO _x , dry, ppmv	520
CO, dry, ppmv	25
HCl, Analyzer, ppmv 3% O ₂	80
HCl, M26, ppmv, 3% O ₂	77

^a Regulated by pilot plant operators to ensure minimal unburned carbon.

**Table 5. Typical Flue Gas Composition Baseline
for FF Tests at Combustor Outlet**

O ₂ , dry, vol % ^a	4.5
CO ₂ , dry, vol %	14.8
SO ₂ , dry, ppmv	575
NO _x , dry, ppmv	525
CO, dry, ppmv	10
HCl, Analyzer, ppmv 3% O ₂	75
HCl, M26, ppmv, 3% O ₂	N/A

^a Regulated by pilot plant operators to ensure minimal unburned carbon.

HCl and SO₂ Reduction

EPA M26 samplings were performed with dry sorbent injection at selected rates throughout the ESP test series to validate the measurement by the HCl analyzer. For each instance, the results between EPA M26 and the HCl analyzer were within 2–4 ppm, proving the validity of HCl measurement by the online HCl analyzer. EPA M26 samples were not taken during the FF test series because of the close agreement of the verification during ESP operation. At the beginning of each day of testing, the HCl analyzer was checked for zero and span with a 90-ppm HCl calibrated gas. The most drift experienced was 3 ppm on the high end in one case.

Table 6 summarizes the results obtained during the testing campaign. The mass concentrations of HCl and SO₂ were calculated from ppmv measurements taken during steady state at each test point. Table 6 also contains a summary of the reduction results for HCl and SO₂ at various sorbent feed rates. Temporal variations of HCl and SO₂ emissions (ppmv at 3% O₂) under different testing conditions are plotted in Figures A1–A8 in Appendix A. Also shown in Figures A1–A8 are the M26 values measured during testing at the selected points.

Reductions of HCl and SO₂ as a function of SR_T of different testing sorbents are plotted in Figures 2 and 3 for the ESP and FF, respectively. For the ESP configuration, as seen in Figure 2, sodium bicarbonate outperformed trona in terms of capturing HCl and SO₂. As for the FF configuration shown in Figure 3, the performance of milled trona (S250) indicated slightly better HCl capture than the unmilled sodium bicarbonate (S350), while the SO₂ removals by S350 and S200 were almost the same in the FF. Only one data point was collected for hydrated lime in the FF test, indicating that much more material was required to attain the same levels of HCl and SO_x capture than that obtained with the sodium-based sorbent. At an injection rate of 1.5 SR_T, hydrated lime only reached 90% HCl removal and 10% SO₂ removal in the FF.

As injected into the flue gas, sorbent was initially heated by the coming flue gas and then cooled as the flue gas temperature decreased with time according to the established temperature-versus-time profile. Assuming the sorbent particles were spherical and fully entrained in the gas flow, the heat transfer between the in-flight sorbent and bulk gas can be described by

$$Nu_D \equiv \frac{hd}{k} = 2 \quad [\text{Eq. 7}]$$

where Nu_D is the Nusselt number, h is the average heat-transfer coefficient, d is the particle diameter, and k is the thermal conductivity of the surrounding gas. Plotted in Figure 4 are the variations of temperature of the sorbents being injected into the flue gas at different locations. Because of the small sizes of the sorbent, the initial heating rate is extremely fast. The temperature of the injected sorbent reached gas temperature within milliseconds.

Table 6. Summary of Acid Gas Reduction Results

ESP																
Sorbent	S200				S250				S350				S450			
Injection Rate, g/Nm ³	0	1.08	1.52	2.77	0	0.87	1.34	1.99	0	0.44	0.87	1.13	0	0.41	0.55	0.71
NSR	0	0.36	0.54	1.21	0	0.27	0.48	1.00	0	0.14	0.34	0.47	0	0.12	0.18	0.27
HCl @3%O ₂ , ppmv	80	14.7	6.8	0.7	76	12.2	2.8	0.1	65.2	15.9	2.1	0.2	70.4	10.3	4	0.1
HCl @3%O ₂ , g/dNm ³	0.121	0.0223	0.0103	0.00106	0.115	0.0185	0.0042	0.00015	0.0989	0.0241	0.0032	0.00030	0.107	0.0156	0.0061	0.00015
HCl, lb/MMBtu	0.084	0.018	0.008	0.0008	0.084	0.015	0.0034	0.00012	0.1	0.0192	0.0025	0.0002	0.085	0.012	0.0048	0.00012
HCl Reduction, %	0.00	81.6	91.5	99.1	0.00	83.9	96.3	99.8	0.00	75.6	96.8	99.7	0.00	85.4	94.3	99.9
SO ₂ @3%O ₂ , ppm)	588	484	453	374	590	521	454	326	576	486	397	371	570	506	469	410
SO ₂ @3%O ₂ , g/dNm ³	1.57	1.29	1.21	1.00	1.57	1.39	1.21	0.87	1.54	1.30	1.06	0.99	1.52	1.35	1.25	1.09
SO ₂ , lb/MMBtu	1.36	1.03	0.96	0.79	1.36	1.11	0.97	0.69	1	1.03	0.84	0.79	1.21	1.08	0.99	0.87
SO ₂ Reduction %	0.00	17.7	22.9	36.4	0.00	11.7	23.0	44.8	0.00	15.6	31.1	35.6	0.00	11.2	17.7	28.1
FF																
Sorbent	S200				S250				S350				Hydrated Lime			
Injection Rate, g/Nm ³	0.00	1.06	1.69	2.56	0.00	0.71	0.80	1.35	0.00	0.39	1.28	1.83	0.00	2.18		
NSR	0	0.30	0.55	0.95	0	0.22	0.26	0.54	0	0.11	0.48	0.89	0	1.49		
HCl @3%O ₂ , ppmv	73	27.7	11.6	1.9	74	23.7	10.1	1	75	49.3	10.8	2.4	75	8.5		
HCl @3%O ₂ , g/dNm ³	0.111	0.042	0.017	0.0029	0.112	0.036	0.015	0.0015	0.114	0.075	0.0164	0.0036	0.114	0.013		
HCl, lb/MMBtu	0.088	0.0335	0.014	0.0023	0.0894	0.029	0.012	0.0012	0.091	0.0597	0.0131	0.0029	0.091	0.0103		
HCl Reduction, %	0.00	62.0	84.1	97.4	0.00	67.9	86.4	98.7	0.00	34.3	85.6	96.8	0.00	88.7		
SO ₂ @3%O ₂ , ppmv	589	559	497	442	573	532	499	407	580	541	407	315	559	503		
SO ₂ @3%O ₂ , g/dNm ³	1.570	1.490	1.325	1.178	1.527	1.418	1.330	1.085	1.546	1.442	1.085	0.840	1.490	1.341		
SO ₂ , lb/MMBtu	1.252	1.189	1.056	0.941	1.217	1.13	1.059	0.865	1.234	1.151	0.864	0.670	1.190	1.071		
SO ₂ Reduction, %	0.00	5.09	15.6	24.9	0.00	7.16	12.9	28.9	0.00	6.72	29.8	45.7	0.00	10.0		

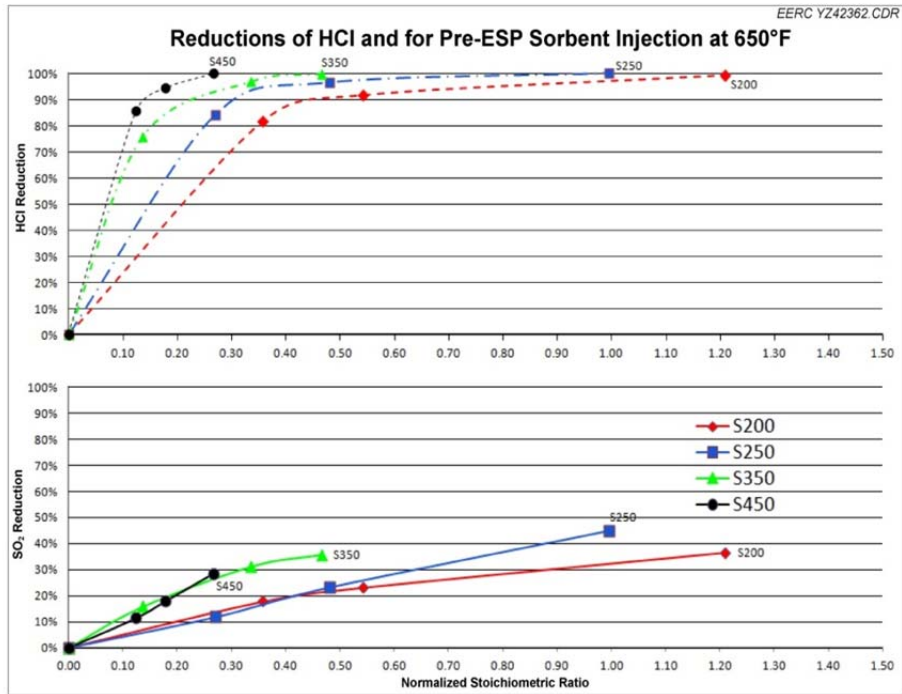


Figure 2. Acid gas reduction with dry sorbent injection in the ESP.

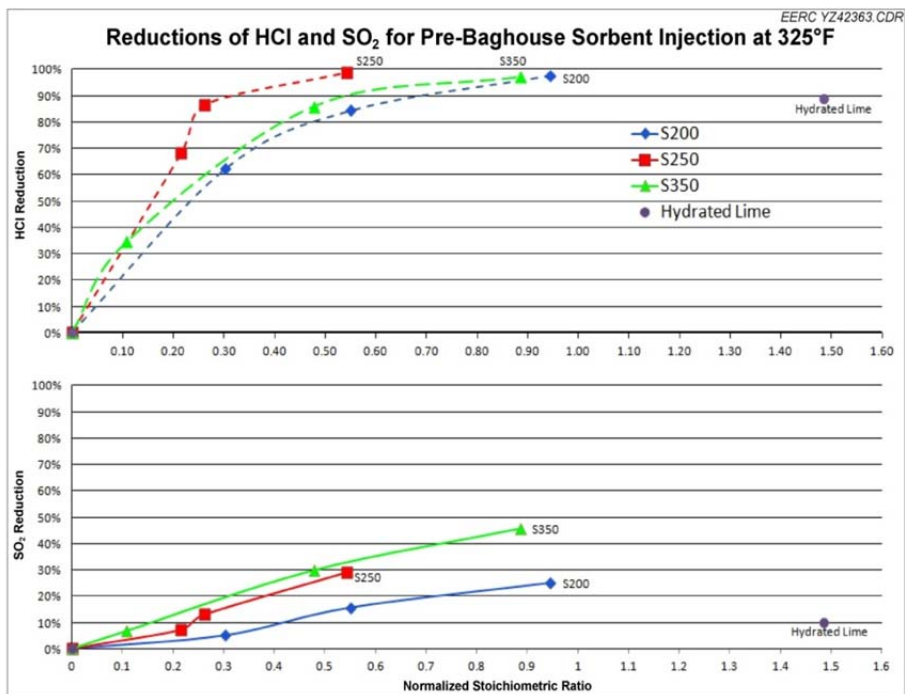


Figure 3. Acid gas reduction with dry sorbent injection in the FF.

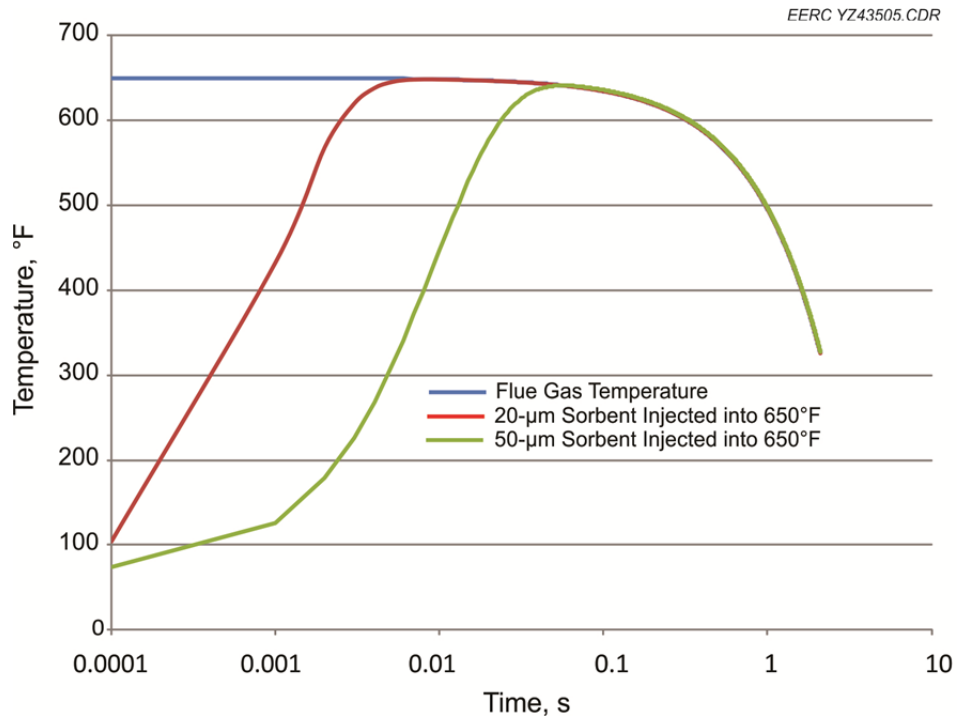


Figure 4a. Temperature variation of sorbent injected at 650°F upstream of the ESP.

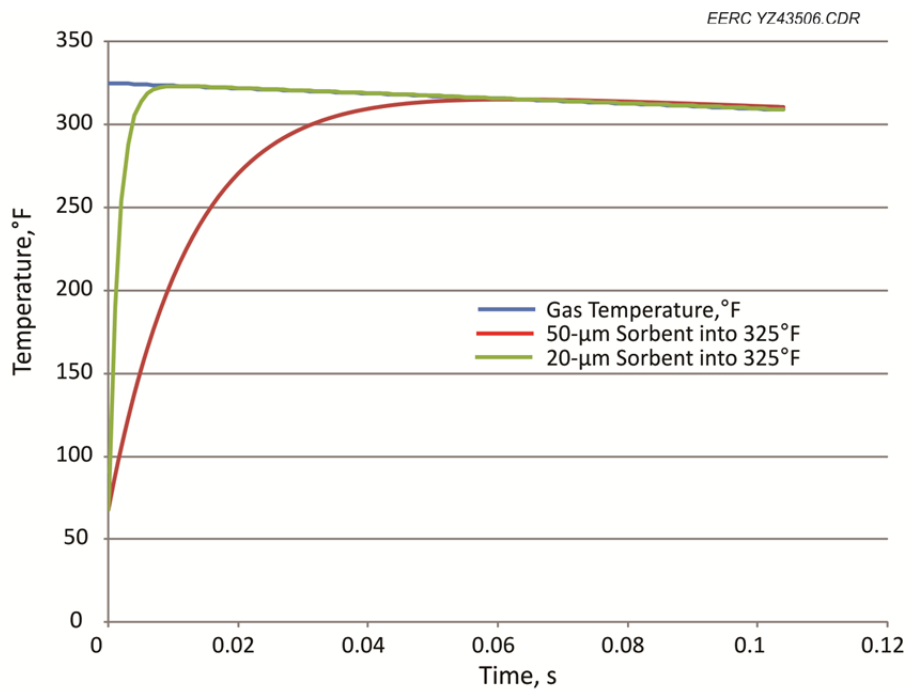


Figure 4b. Temperature variation of sorbent injected at 325°F upstream of the FF.

Heating rate will affect the decomposition behavior of trona. Plotted in Figure 5 are the weight changes of S250 under the heating rates of 20°C/min and 100°C/min, respectively. Under the 100°C/min heating rate, trona particles began decomposition at an earlier stage in terms of time and temperature, and d_{50} of the decomposed particle was 19.6 μm , smaller than the d_{50} of 22 μm obtained under 20°C/min condition. In summary, smaller sorbent size and higher injection temperature would result in a faster heating rate that would further reduce the actual size of sorbent in flow.

The heat-transfer calculation and measurement of particle size after thermogravimetry analysis (TGA) may explain the reason for the different size effect on capturing HCl and SO₂ at the ESP and FF, respectively. Under the ESP condition, all different-sized sorbents experienced a fast heating process, and the actual sizes decreased to some degree. However, the actual size difference between them would at least be maintained the same as the parent particles. As a result, the smaller-sized sorbents of S250 and S450 performed better than the corresponding unmilled S200 and S350, respectively. It should be noted that the sorbent size effect was more significant in adsorbing HCl than SO₂, most likely because of the different reactivities of HCl and SO₂ to the sorbent. For the FF test, where sorbent injection had taken place at the lower temperature of 325°F, S250 most likely still decreased its size as a result of a fast heating process, which favors small particles. Therefore, the performance of S250 in the FF test was at the same level as that in the ESP test. The fact that a higher injection temperature did not appear to have any real effect on milled trona (S250) suggests that the change of sorbent size driven by temperature is possibly limited by the initial particle size. However, the S200 had a size large enough that the relatively slow heating process may not have broken down the parent particle as happened under the ESP condition. Therefore, S200 was less effective at capturing HCl and SO₂ within the FF than in the ESP.

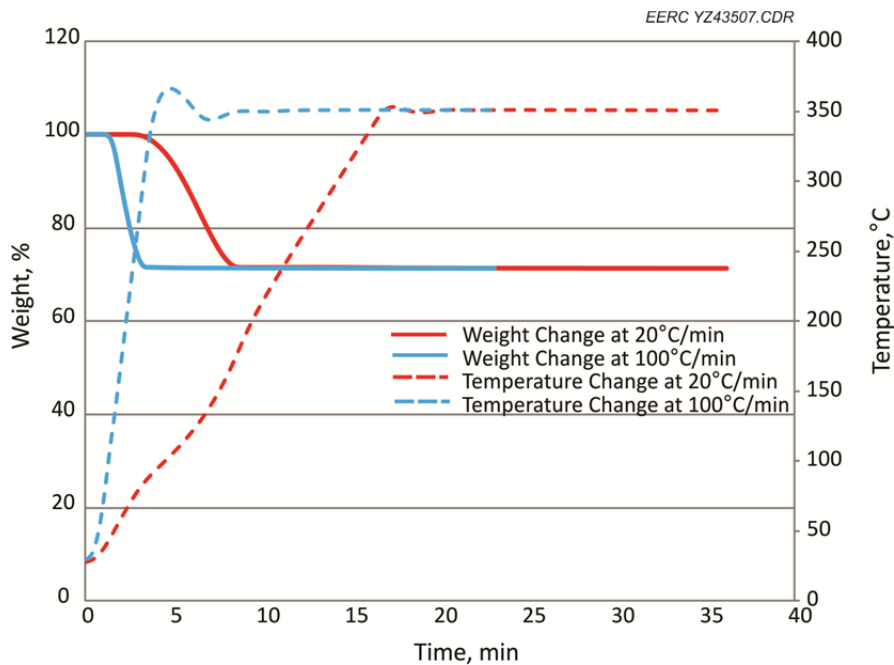


Figure 5. TGA results of S250 under heating rates of 20°C/min and 100°C/min.

The unmilled sodium bicarbonate S350 performed better in the ESP than in the FF, mainly because the activated process occurred in the high-temperature injection during the ESP test.

NO_x Discussion

NO_x was reduced somewhat during sorbent injection. There is some natural NO_x reduction in the system from the combustor to the stack without sorbent injection (3% for ESP configurations and 2% for FF configurations). Comparing corrected NO_x at the combustor outlet and the stack, it can be seen in Figure 6 that there is a natural 2%–3% reduction in NO_x. However, in the ESP configuration, up to a 20% reduction in NO_x was observed during trona injection and up to 19% reduction during S350 injection. The FF configuration did not experience NO_x reduction rates as high as the ESP configuration, but they were higher than the system baseline reduction. The highest NO_x reduction rate observed in a FF configuration was 10%.

EPA Regulations

This test campaign was performed because of a new set of EPA regulations involving the emission of acid gases. These emission guidelines relevant to existing plants are shown in Table 7. In Row B, it is observed that the acid gas regulation is for either HCl or SO₂. The CAPP coal used in this study had a heating value of 11,496 Btu/lb. The upper limit for HCl emission using a coal greater than 8300 Btu/lb is 0.002 lb/MMBtu. The upper limit for SO₂ emission using a coal greater than 8300 Btu/lb is 0.2 lb/MMBtu.

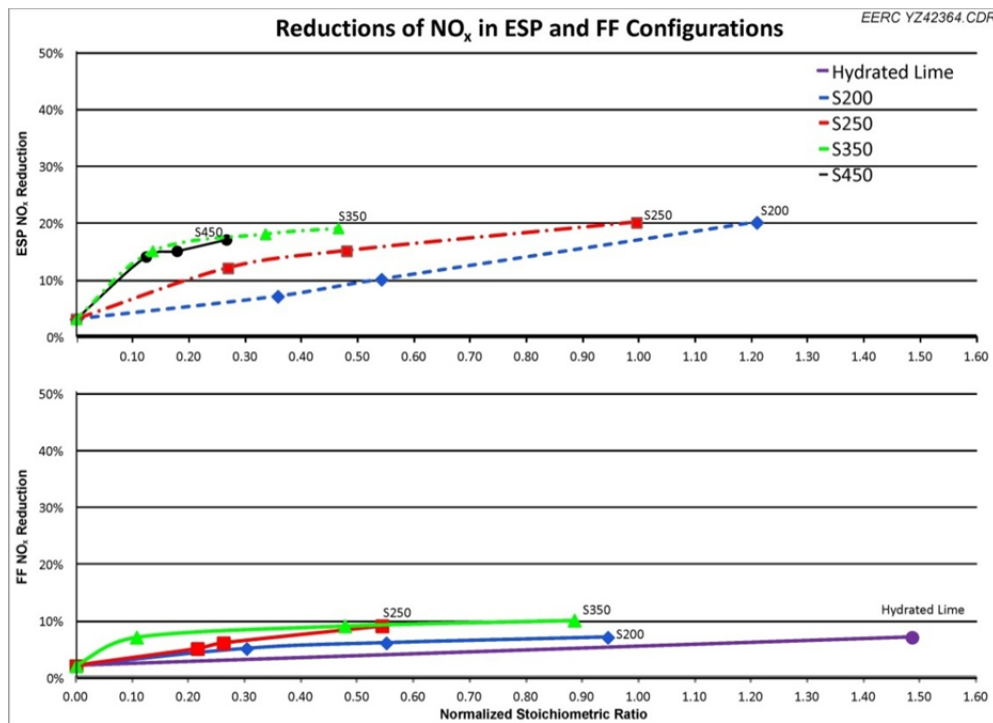


Figure 6. NO_x reduction in ESP and FF configurations.

Table 7. EPA Regulation on HCl and SO₂

	Unit for Coal >8300 Btu/lb		Unit for Coal <8300 Btu/lb	
A	Total PM	0.030 lb/MMBtu	Total PM	0.030 lb/MMBtu
	OR		OR	
	Total non-Hg HAP metals	0.00004 lb/MMBtu	Total non-Hg HAP metals	0.00004 lb/MMBtu
B	HCl	0.002 lb/MMBtu	HCl	0.002 lb/MMBtu
	OR		OR	
	SO ₂	0.2 lb/MMBtu	SO ₂	0.2 lb/MMBtu
C	Hg	1.0 lb/TBtu	Hg	4.0 lb/TBtu

The acid gas reduction data for 650°F injection before the ESP is shown in Figure 7. SO₂ was not reduced to a level below the EPA limit for any of the sorbents or injection rates tested. HCl was reduced below the EPA limit using S200, S250, S350, and S450 for the highest injection rates tested for each sorbent. Trona requires two to three times higher NSR than sodium bicarbonate to reach the EPA limits.

The acid gas reduction data for 325°F injection before the FF is shown in Figure 8. SO₂ was not reduced to a level below the EPA limit for any of the sorbents or injection rates tested. HCl was reduced below the EPA limit in the FF configuration only in the case of S250 injection

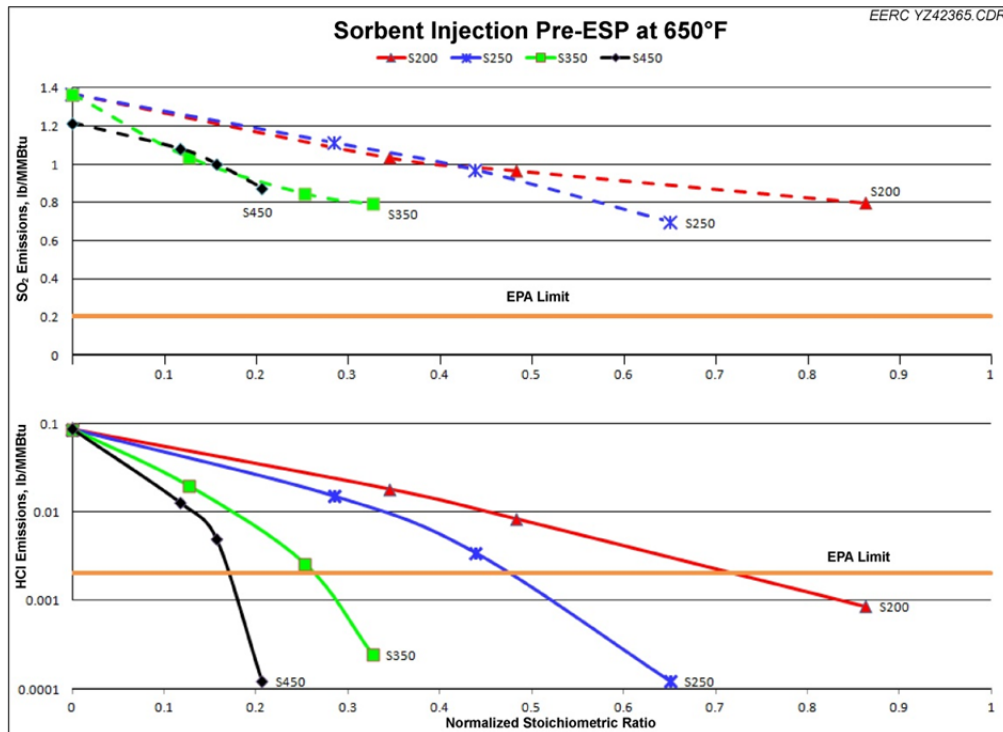


Figure 7. ESP acid gas reduction to EPA limits.

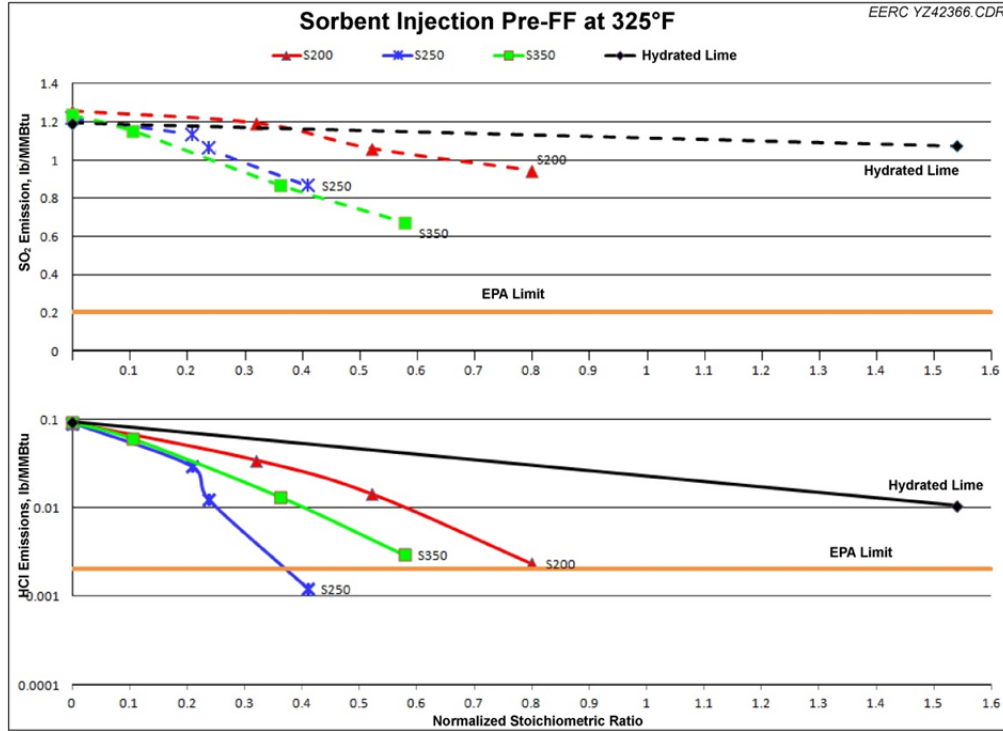


Figure 8. FF acid gas reduction to EPA limits.

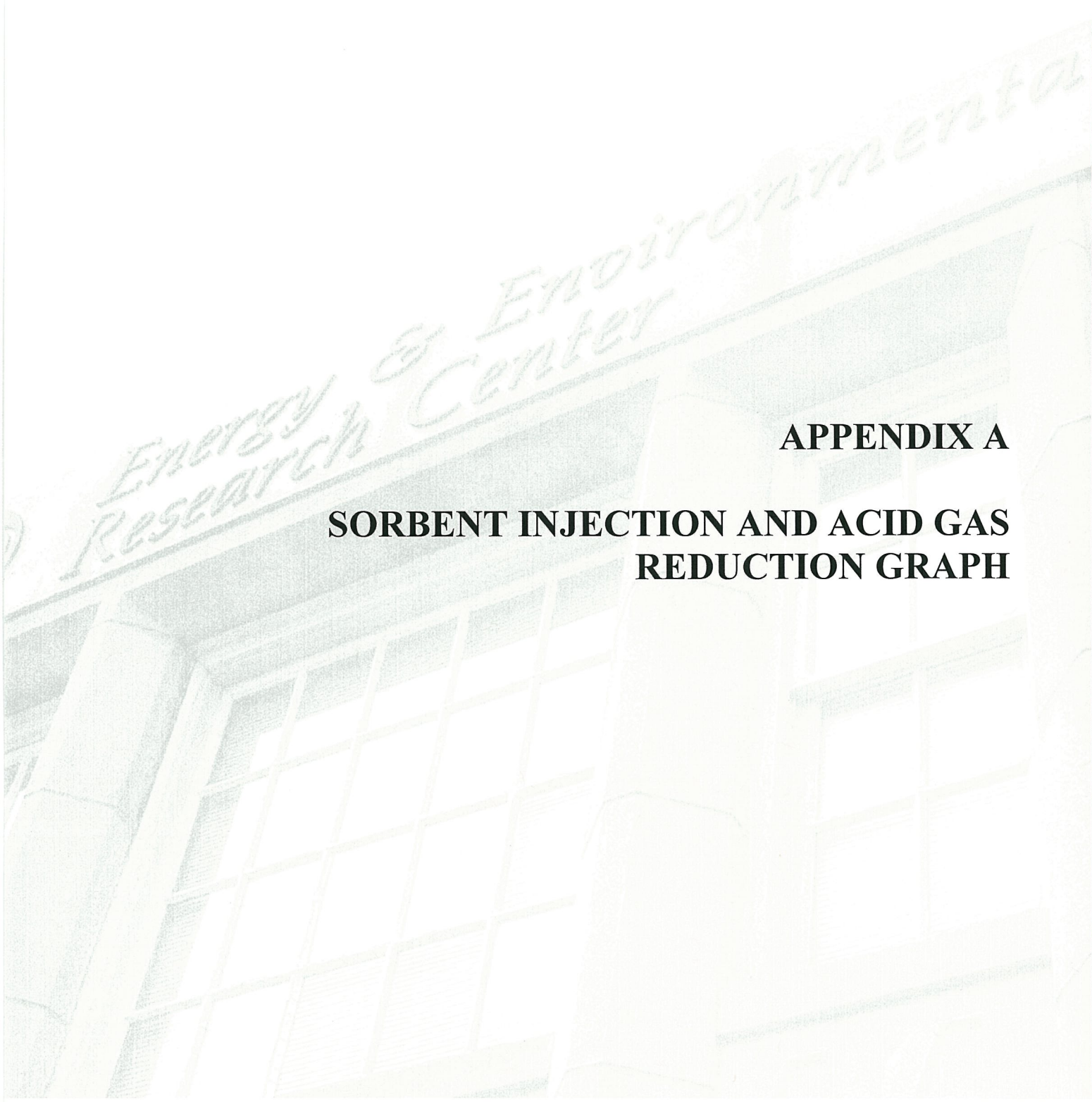
at a NSR of 0.5. S350 and S200 came close to meeting the limit at the tested NSR injection rates of 0.9 and 0.98, respectively.

CONCLUSIONS

The HCl online analyzer used to generate the bulk of these data agreed well with the M26 samples taken during testing under different conditions. The estimated HCl emissions based upon the chlorine content of the coal agreed well with the measurement of both M26 and the continuous HCl analyzer in the baseline test.

For combustion of CAPP coal using an ESP capture device, this test campaign was able to achieve the EPA limits on HCl emissions in the case of the four sorbents used, S200, S250, S350, and S450, while sodium bicarbonate outperformed trona in capturing HCl. Smaller-sized sorbents of S250 and S450 have better performance than their corresponding unmilled S200 and S350, respectively. Meanwhile, the sorbent size effect was more significant in adsorbing HCl than SO₂.

Of the sorbents tested in the FF configuration, only S250 was able to reach the EPA HCl limit. SO₂ emission limits established by EPA were not met with any the sorbents at the injection rates tested. Because of the less efficient activation at 325°F than at 625°F, both trona and sodium bicarbonate need higher injections in the FF tests to achieve the same levels of removal of SO₂ and HCl in the ESP test.



APPENDIX A

**SORBENT INJECTION AND ACID GAS
REDUCTION GRAPH**

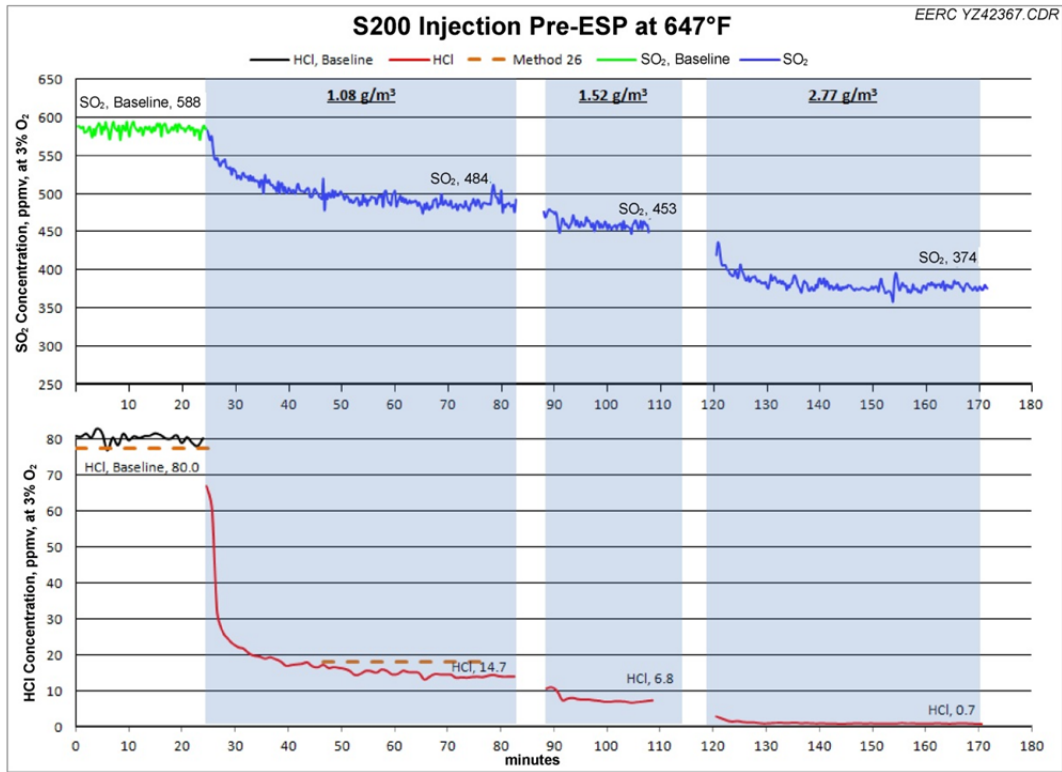


Figure A-1. S200 pre-ESP injection results.

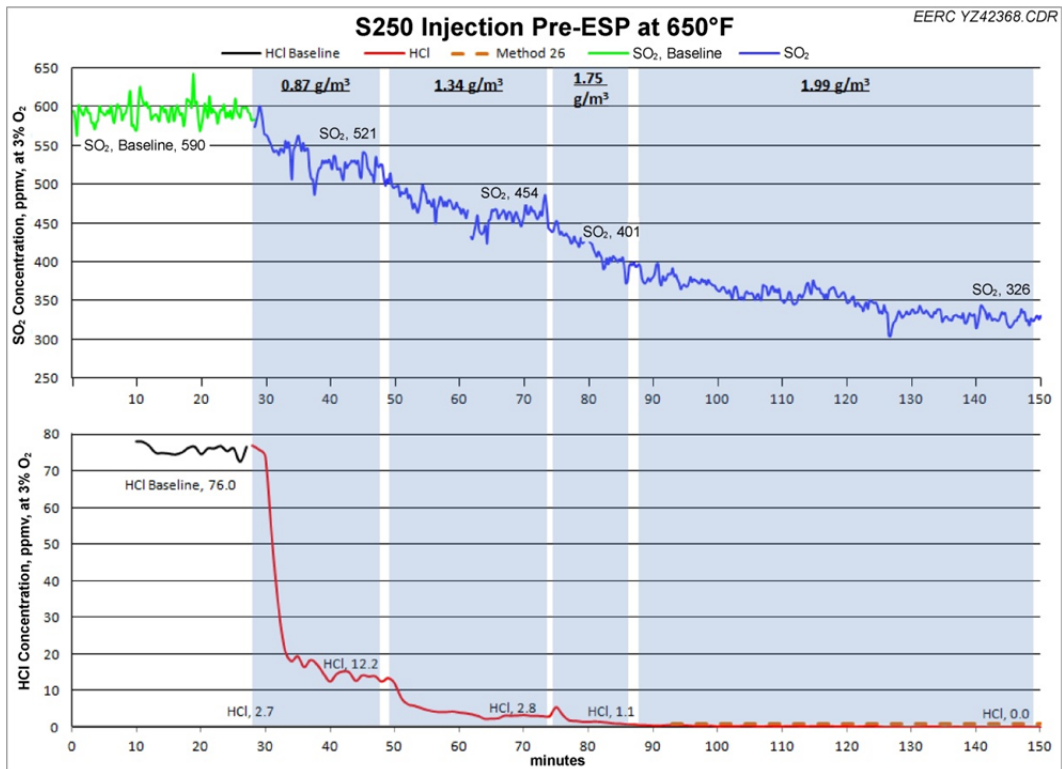


Figure A-2. S250 pre-ESP injection results.

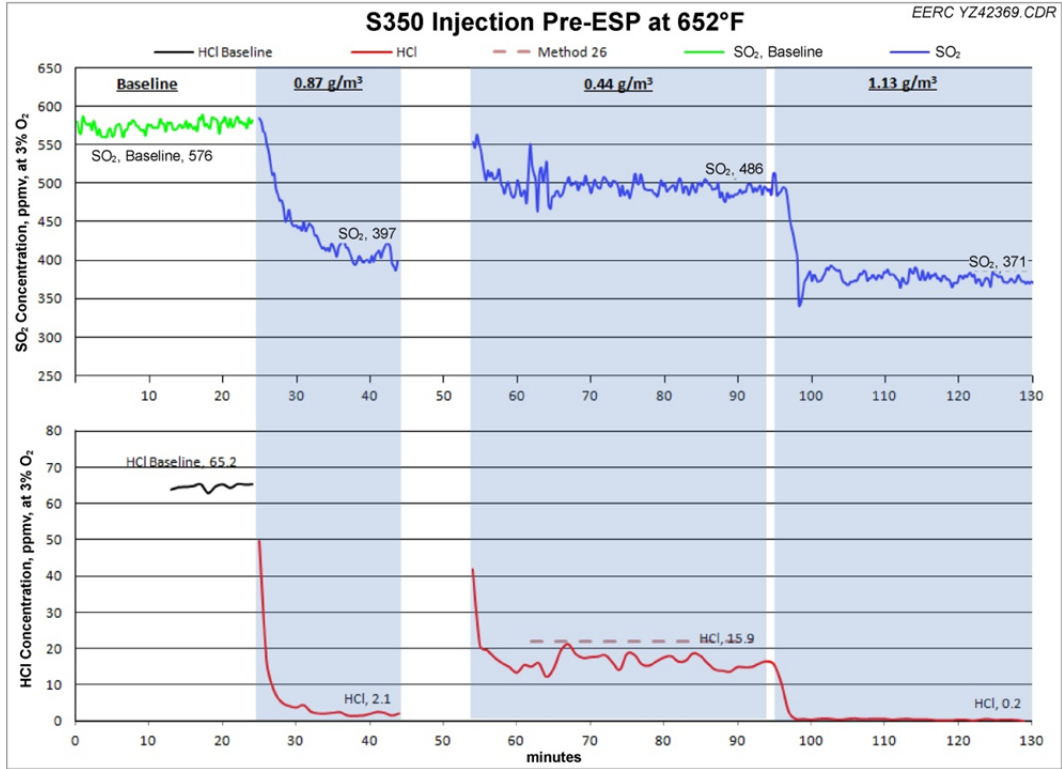


Figure A-3. S350 pre-ESP injection results.

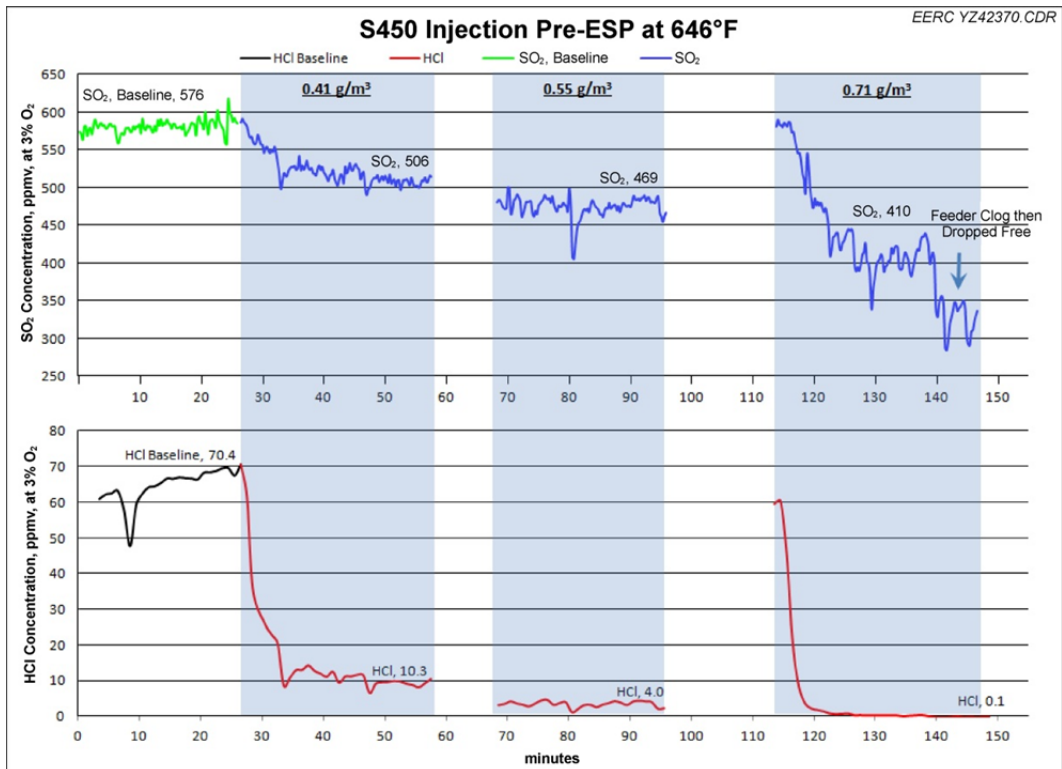


Figure A-4. S450 pre-ESP injection results.

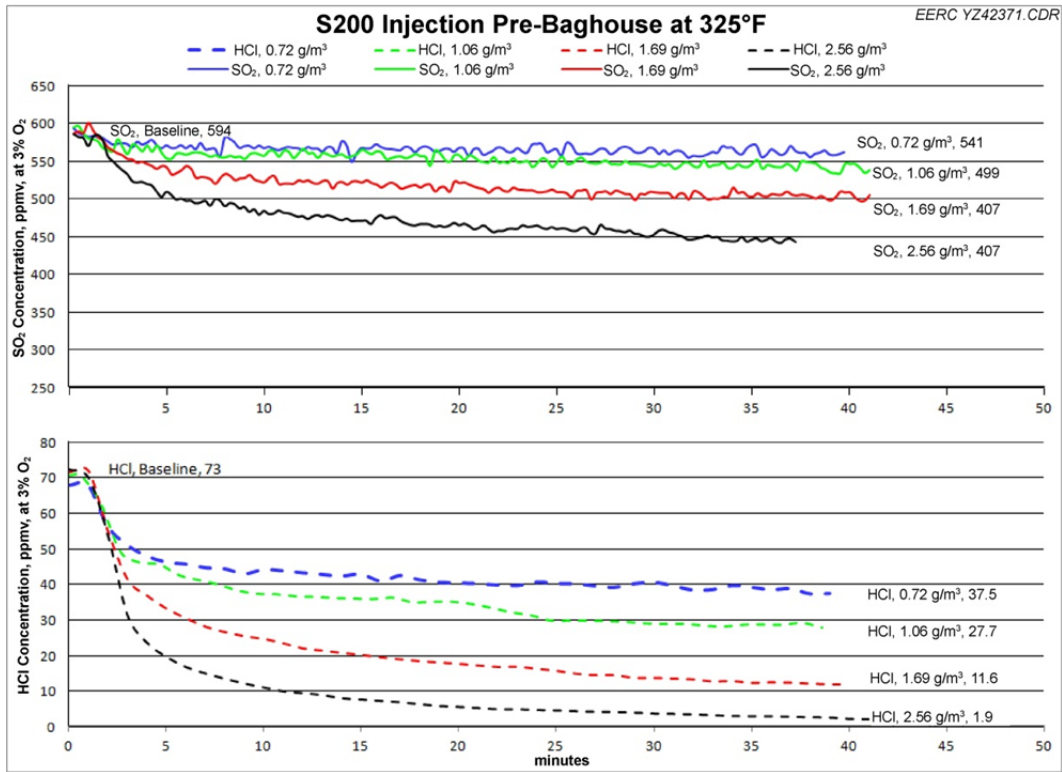


Figure A-5. S200 pre-FF injection results.

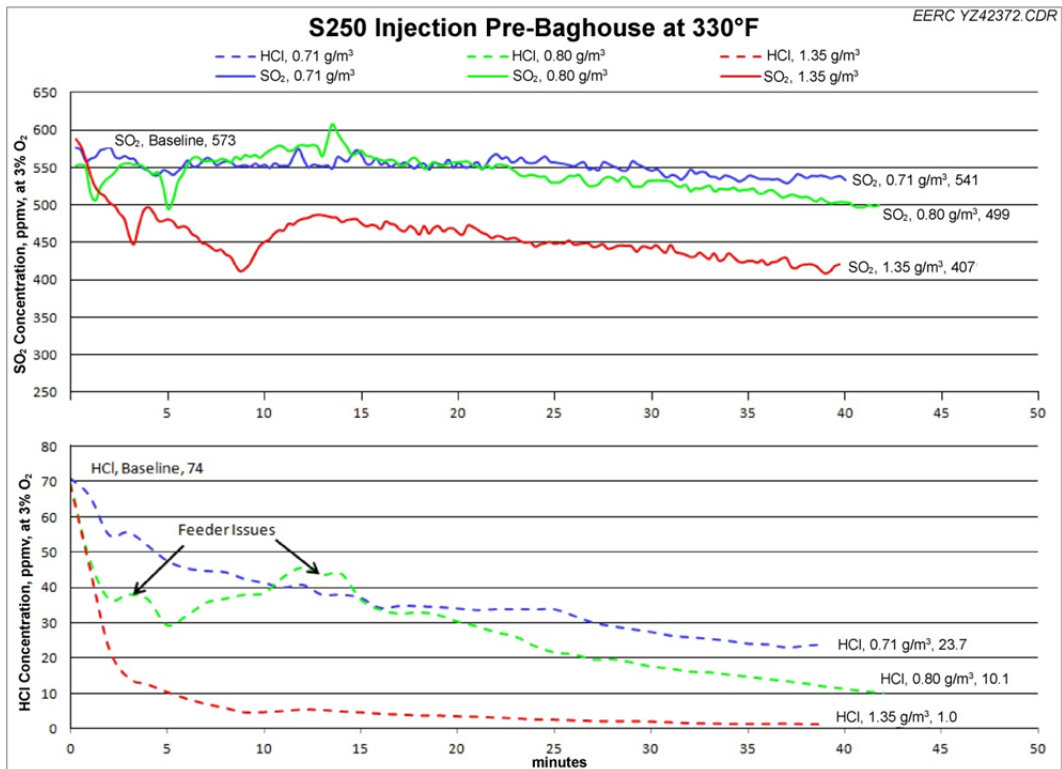


Figure A-6. S250 pre-FF injection results.

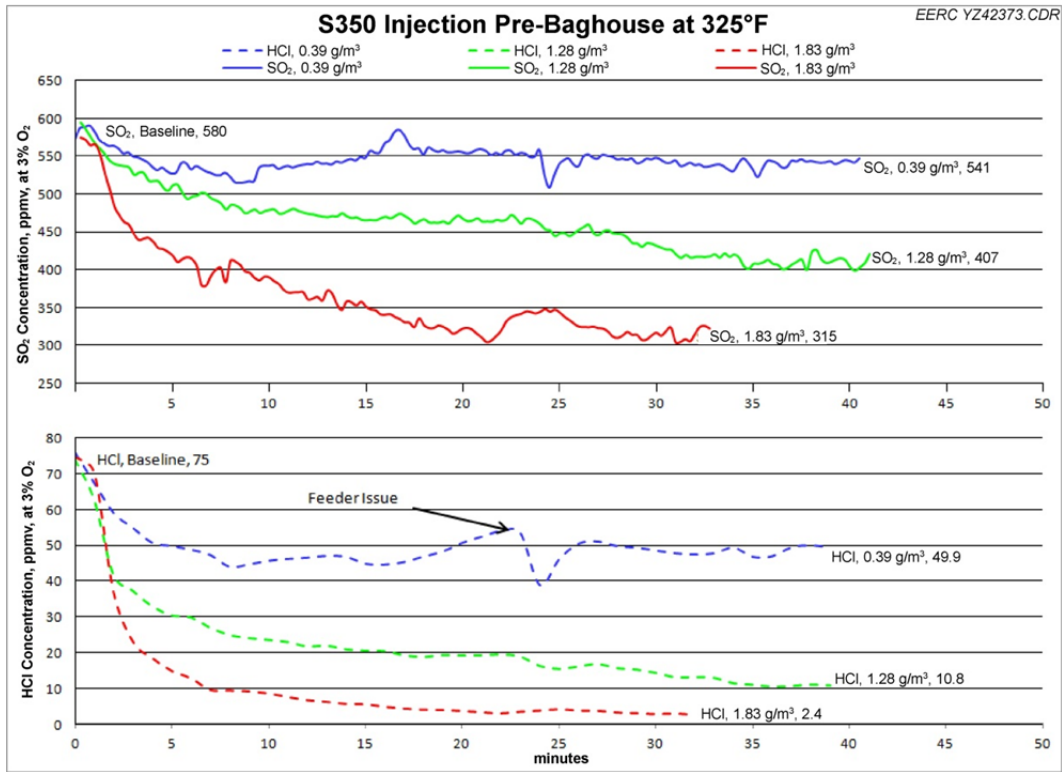


Figure A-7. S350 pre-FF injection results.

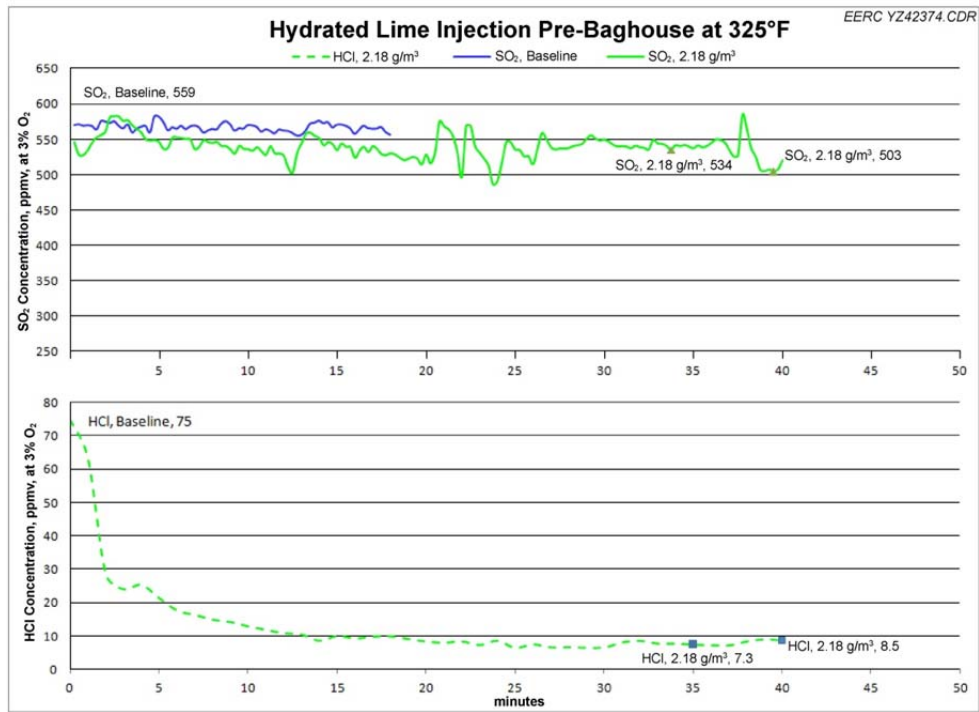
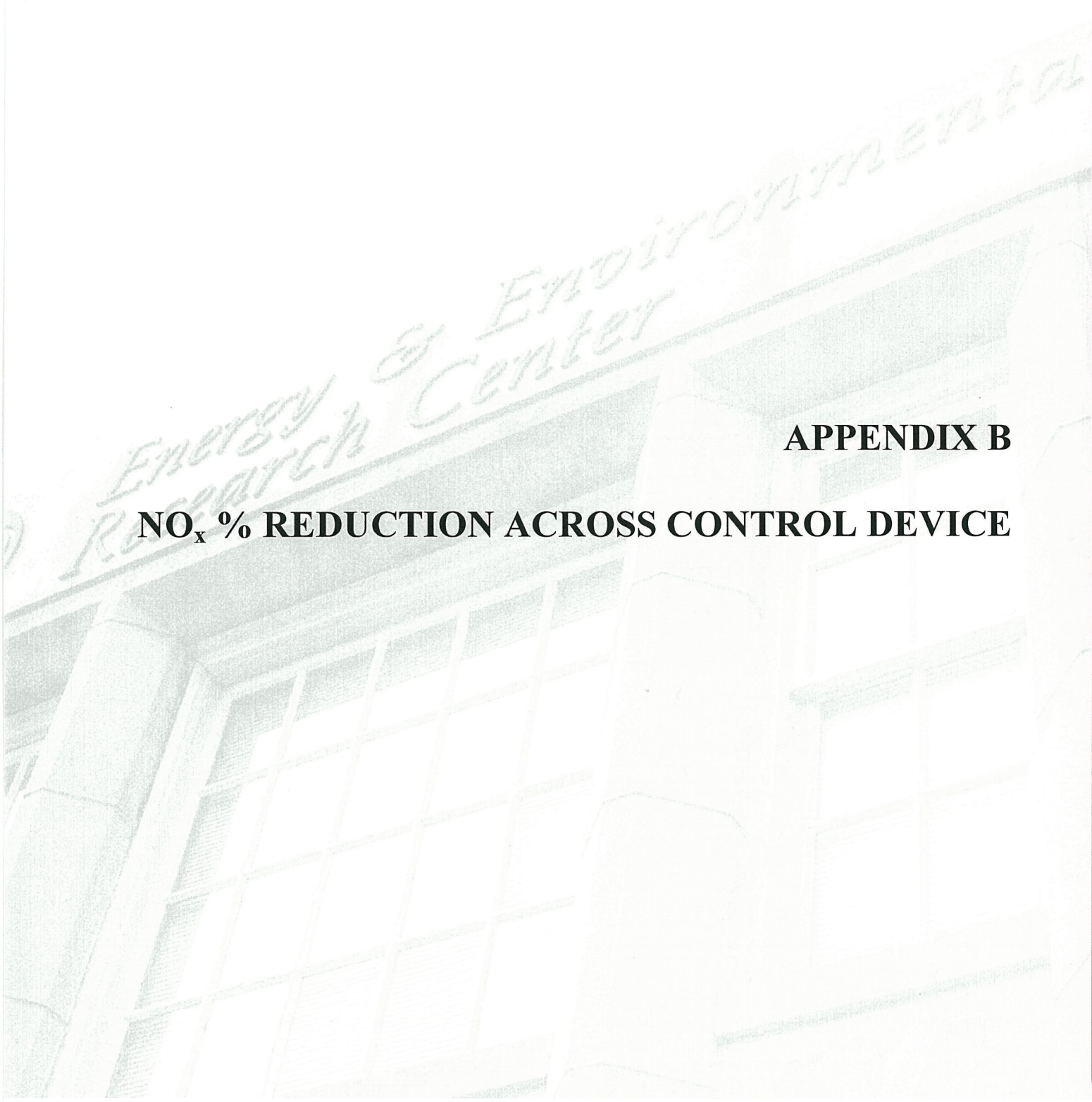


Figure A-8. Hydrated lime pre-FF injection results.



APPENDIX B

NO_x % REDUCTION ACROSS CONTROL DEVICE

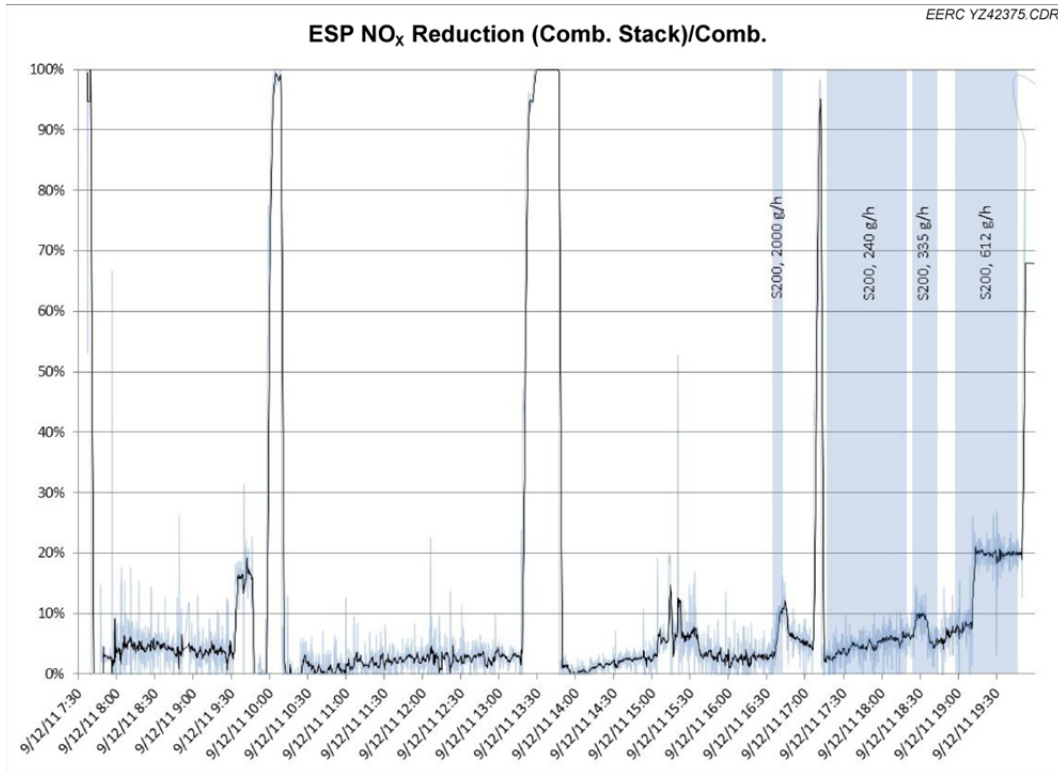


Figure B-1. ESP NO_x reduction (1).

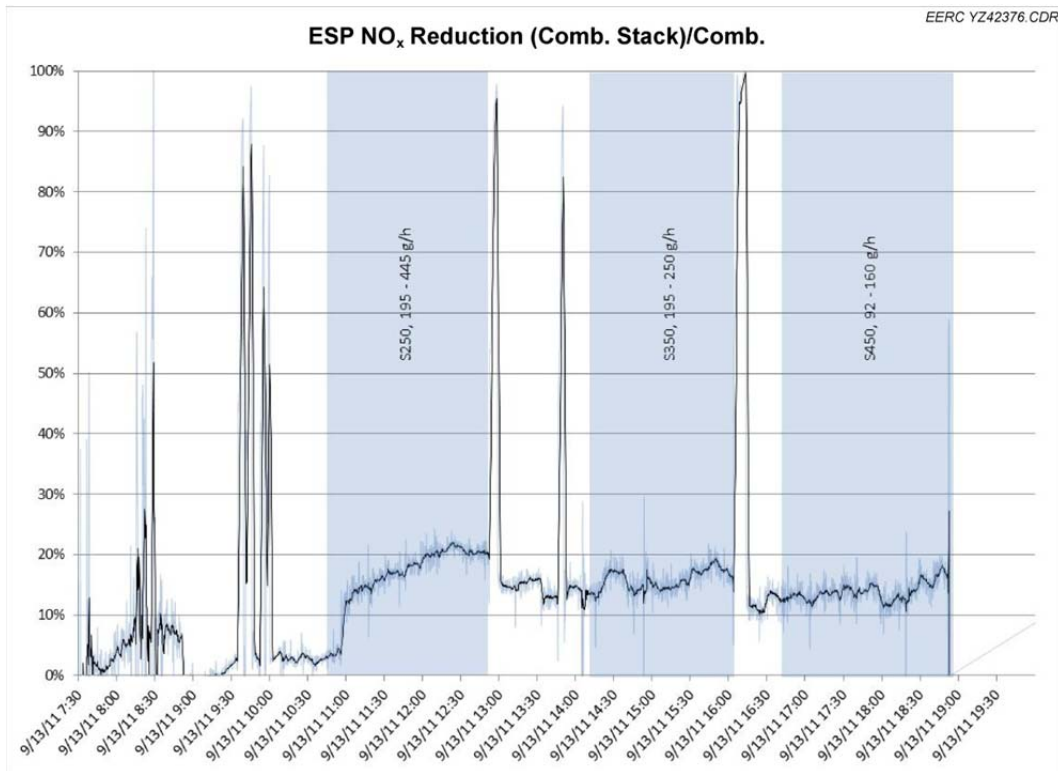


Figure B-2. ESP NO_x reduction (2).

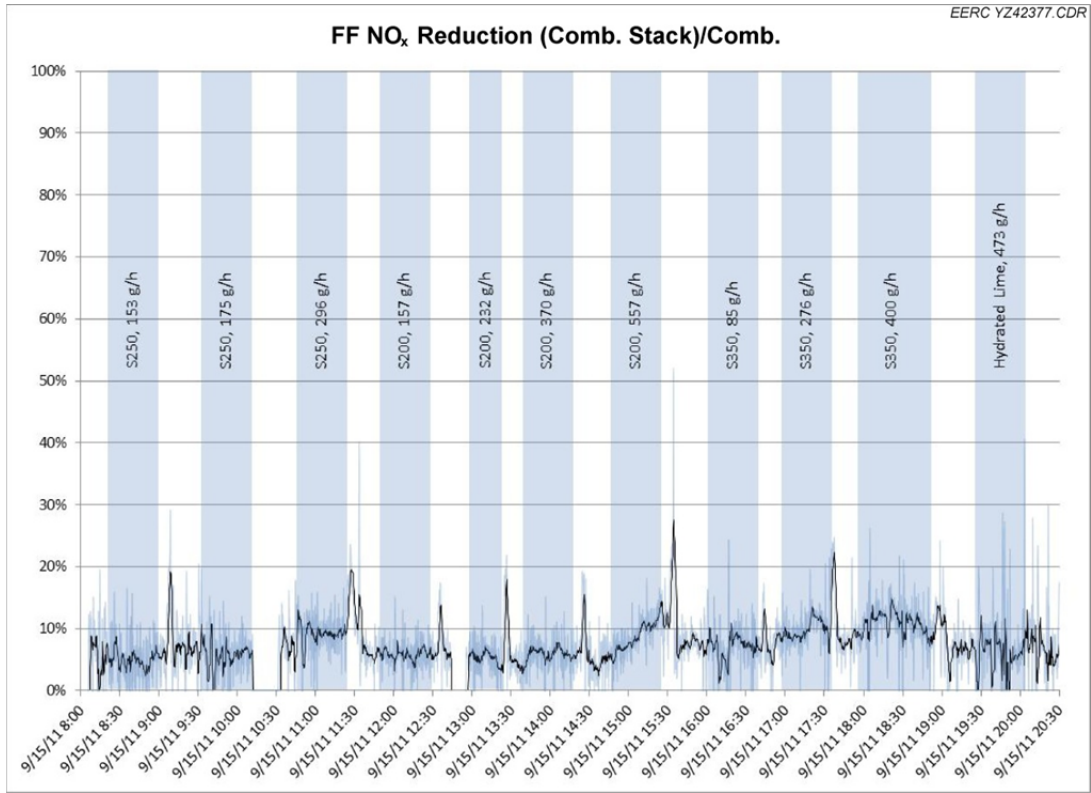


Figure B-3. FF NO_x reduction.

ANEXO 2

Límites de Emisión BATC EU para LCP (Large Combustion Plants)

LCP BAT – AEL >50<100 MWt

LCP BATC BAT-AEL for new plant > 50 < 100 MWt

Pollutants	Section	10.2.1		10.3.1		10.3.2		10.4.2		10.5				10.7			
		Fuels		coal & lignite		liquid fuels boilers		Liquid fuels engines		Iron&steel gases		multifuels utility boilers in Chemical				Biomass or peat	
				min	max	min	max	min	max	min	max	Liquid + gas		only gas		min	max
Net elec efficiency	%	36,5 40		>36,4		> 41,5 44,5								33,5 > 38			
Net total fuel utilisation	%	75 97		80 96										73 99			
NOx	mg/Nm ³	100	150	75	200	115	225	15	65	30	85	20	80	70	150		
NH3	mg/Nm ³	ND	ND					ND	ND					ND			
CO	mg/Nm ³	30	140	10	30	50	175	5	35	5	30	5	30	30	250		
SOx	mg/Nm ³	150	200	50	175	45	100	25	150	10	110	10	110	15	70		
HCl	mg/Nm ³	1	6	ND				ND		1	7	2	15	1	7		
HF	mg/Nm ³	1	3	ND				ND		1	2	1	2	<1			
Dust	mg/Nm ³	2	5	2	10	5	10	2	7	2	5	2	5	2	5		
Heavy metals	mg/Nm ³	ND		ND				ND									
Hg	µgNm ³	1	3 5 ⁽¹⁾	ND				ND						1	5		
Dioxines/furanes	ng/nm ³ (teq)	ND		ND				ND		0,012	0,036	0,012	0,036	ND			
TOC	mg/Nm ³	ND		ND		10	40	ND		0,6	12	0,6	12	ND			

LCP BATC BAT-AEL for existing plant > 50 < 100 MWt

Pollutants	Section	10.2.1		10.3.1		10.3.2		10.4.2		10.5				10.7			
		Fuels		coal & lignite		liquid fuels boilers		Liquid fuels engines		Iron&steel gases		multifuels utility boilers in Chemical				Biomass or peat	
				min	max	min	max	min	max	min	max	Liquid + gas		only gas		min	max
Net elec efficiency	%	31,5 39,5		>35,6		37,4 38,3		44,5						33,5 > 38			
Net total fuel utilisation	%	75 97		80 96										73 99			
NOx	mg/Nm ³	100	270	150	270	125	625	20	100	80	290	70	100	70	225		
NH3	mg/Nm ³	ND	ND														
CO	mg/Nm ³	30	140	10	30	50	175	5	100	5	30	5	30	30	250		
SOx	mg/Nm ³	150	360	50	175	100	200	25	150	10	110	10	110	15	100		
HCl	mg/Nm ³	2	10	ND				ND		2	15	2	15	1	15		
HF	mg/Nm ³	1	3	ND				ND		1	3	1	3	<1,5			
Dust	mg/Nm ³	2	18	2	20	5	35	2	7	2	15	2	15	2	15		
Heavy metals	mg/Nm ³	ND		ND				ND									
Hg	µgNm ³	1 2 ⁽¹⁾	9 10 ⁽¹⁾	ND				ND						1	5		
Dioxines/furanes	ng/nm ³ (teq)	ND		ND				ND		0,012	0,036	0,012	0,036	ND			
TOC	mg/Nm ³	ND		ND		10	40	ND		0,6	12	0,6	12	ND			

* Lecho Fluido o Lignito

(1) Lignito

LCP BAT – AEL >100<300 MWt

LCP BATC BAT-AEL for new plant > 100 < 300 MWt

Pollutants	Section	10.2.1		10.3.1		10.3.2		10.4.2		10.5				10.7	
		Fuels		coal & lignite		liquid feuls		Liquid fuels engines		Iron&steel gases		multifuels utility boilers in Chemical		Biomass or peat	
				min	max	min	max	min	max	min	max	Liquid + gas		only gas	
Net elec efficiency	%	36,5	40	>36,4		> 41,5		44,5						33,5	> 38
Net total fuel utilisat	%	75	97	80	96									73	99
NOx		50	100	45	75	115	225	15	65	30	85	20	80	50	140
NH3	mg/Nm ³							ND	ND						ND
CO	mg/Nm ³	30	100	10	20	50	175	5	35	5	30	5	30	30	160
SOx	mg/Nm ³	80	150	50	175	45	100	25	150	10	110	10	110	<10	50
HCl	mg/Nm ³	1	3	ND				ND		1	5	2	15	1	5
HF	mg/Nm ³	1	2	ND				ND		1	2	1	2	<1	
Dust	mg/Nm ³	2	5	2	10	5	10	2	7	2	5	2	5	2	5
Heavy metals	mg/Nm ³	ND		ND				ND							
Hg	µgNm ³	1	3 5 ⁽¹⁾	ND				ND						1	5
Dioxines/furanes	pg/nm ³ (teq)	ND		ND				ND		0,012	0,036	0,012	0,036	ND	
TOC	mg/Nm ³	ND		ND		10	40	ND		0,6	12	0,6	12	ND	

LCP BATC BAT-AEL for existing plant > 100 < 300 MWt

Pollutants	Section	10.2.1		10.3.1		10.3.2		10.4.2		10.5				10.7	
		Fuels		coal & lignite		liquid feuls boilers		Liquid fuels engines		Iron&steel gases		multifuels utility boilers in Chemical		Biomass or peat	
				min	max	min	max	min	max	min	max	Liquid + gas		only gas	
Net elec efficiency	%	31,5	39,5	>35,6		37,4		38,3		44,5				33,5	> 38
Net total fuel utilisat	%	75	97	80	96									73	99
NOx	mg/Nm ³	100	180	45	110	125	625	20	100	80	290	70	100	50	180
NH3	mg/Nm ³														
CO	mg/Nm ³	30	100	10	20	50	175	5	100	5	30	5	30	30	160
SOx	mg/Nm ³	95	200	50	175	100	200	25	150	10	110	10	110	10	70
HCl	mg/Nm ³	<1	5	ND				ND		2	9	2	9	1	9
HF	mg/Nm ³	1	2	ND				ND		1	3	1	3	<1	
Dust	mg/Nm ³	2	14	2	20	5	35	2	7	2	15	2	15	2	12
Heavy metals	mg/Nm ³	ND		ND				ND							
Hg	µgNm ³	1 2 ⁽¹⁾	9 10 ⁽¹⁾	ND				ND						1	5
Dioxines/furanes	pg/nm ³ (teq)	ND		ND				ND		0,012	0,036	0,012	0,036	ND	
TOC	mg/Nm ³	ND		ND		10	40	ND		0,6	12	0,6	12	ND	

* Lecho Fluido o Lignito

(1) Lignito

LCP BAT – AEL >300 MWt

LCP BATC BAT-AEL for new plant > 300 MWt

Pollutants	Section	10.2.1		10.3.1		10.3.2		10.4.2		10.5				10.7	
		Fuels		liquid feuls		Liquid fuels engines		Iron&steel gases		multifuels utility boilers in Chemical				Biomass or peat	
		coal & lignite		liquid feuls		Liquid fuels engines		Iron&steel gases		Liquid + gas		only gas		Biomass or peat	
Net elec efficiency	%	45	46	>36,4		> 41,5		44,5						33,5	> 38
Net total fuel utilisation	%	75	97	80	96									73	99
NOx	mg/Nm ³	50* 65	85	45	75	115	225	15	65	30	85	20	80	40	140
NH3	mg/Nm ³							ND	ND					ND	
CO	mg/Nm ³	5	100	10	20	50	175	5	35	5	30	5	30	30	80
SOx	mg/Nm ³	10 (20) ¹	75	35	50	45	100	25	150	10	110	10	110	10	35
HCl	mg/Nm ³	1	3	ND				ND		1	5	2	15	1	5
HF	mg/Nm ³	1	2	ND				ND		1	2	1	2	<1	
Dust	mg/Nm ³	2	5	2	5	5	10	2	7	2	5	2	5	2	5
Heavy metals	mg/Nm ³	ND	ND	ND				ND						<1	
Hg	µgNm ³	1	2 4 ⁽¹⁾	ND				ND						1	5
Dioxines/furanes	pg/nm ³ (teq)	ND	ND	ND				ND		0,012	0,036	0,012	0,036	ND	
TOC	mg/Nm ³	ND	ND	ND		10	40	ND		0,6	12	0,6	12	ND	

LCP BATC BAT-AEL for existing plant > 300 MWt

Pollutants	Section	10.2.1		10.3.1		10.3.2		10.4.2		10.5				10.7	
		Fuels		liquid feuls boilers		Liquid fuels engines		Iron&steel gases		multifuels utility boilers in Chemical				Biomass or peat	
		coal & lignite		liquid feuls boilers		Liquid fuels engines		Iron&steel gases		Liquid + gas		only gas		Biomass or peat	
Net elec efficiency	%	31,5	39,5	>35,6	37,4	38,3		44,5						33,5	> 38
Net total fuel utilisation	%	75	97	80	96									73	99
NOx	mg/Nm ³	85	150	45	110	125	625	20	100	80	290	70	100	40	150
NH3	mg/Nm ³													ND	
CO	mg/Nm ³	5	100	10	20	50	175	5	100	5	30	5	30	30	80
SOx	mg/Nm ³	10 (20) ¹	130 (180) ¹	50	110	100	200	25	150	10	110	10	110	10	50
HCl	mg/Nm ³	<1	5	ND				ND		2	9	2	9	1	5
HF	mg/Nm ³	1	2	ND				ND		1	3	1	3	ND	
Dust	mg/Nm ³	2	10	2	10	5	35	2	7	2	10	2	10	2	10
Heavy metals	mg/Nm ³	ND	ND	ND				ND						<1	
Hg	µgNm ³	1 2 ⁽¹⁾	4 10 ⁽¹⁾	ND				ND						1	5
Dioxines/furanes	pg/nm ³ (teq)	ND	ND	ND				ND		0,012	0,036	0,012	0,036	ND	
TOC	mg/Nm ³	ND	ND	ND		10	40	ND		0,6	12	0,6	12	ND	

* Lecho Fluido o Lignito

(1) Lignito