Combustion & Catalysis Laboratory

WTERT
Waste-To-Energy Research and Technology Council

WTERT research

Marco J. Castaldi
Chemical Engineering Department
City University of New York (CCNY)
The City University of New York (CUNY)

Director of Research: WTERT
Associate Director, Earth Engineering Center

WTERT 2012 Bi-Annual Meeting, Columbia University
NEW YORK CITY, OCTOBER 18 & 19, 2012

the City College of New York

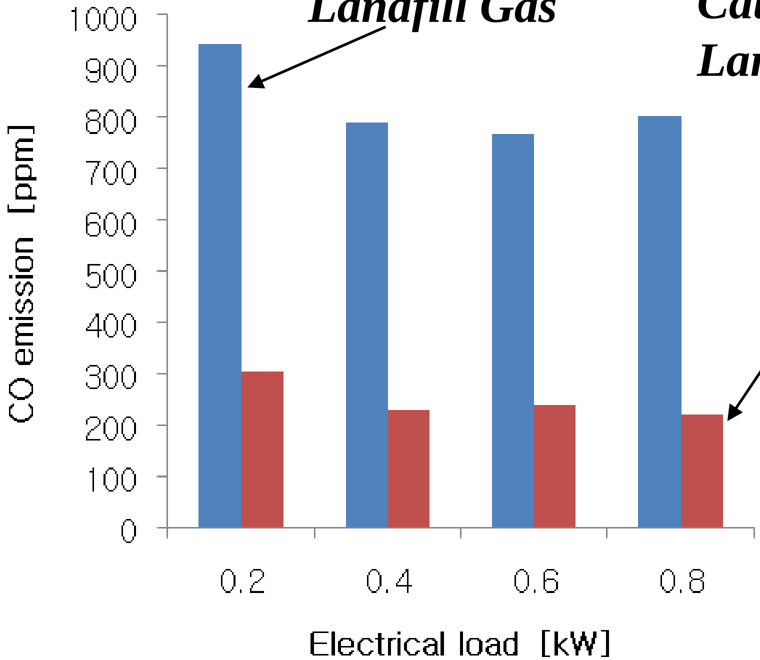
2010 – 2012 Activities

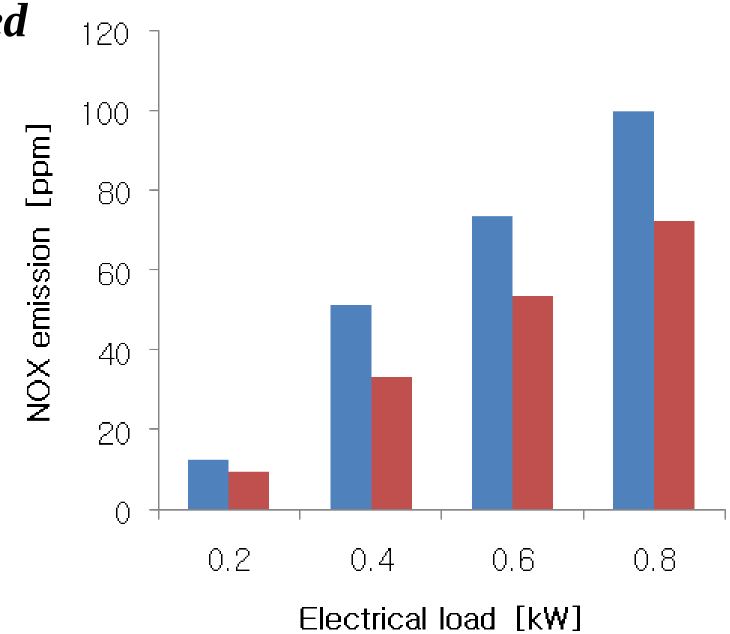
- LFGTE – Understanding of Cl impurities in LFG, Engine Testing
- NOx modeling – Fuel-N conversion to NO precursors
- Corrosion – Impact of sulfur and type of salt coverage
- Ash – New uses: environmental catalytic reactions
- General Activities: WTE Book & Course; WTE Nigeria, Bulgaria

Energy from Landfill Gas

Landfill Gas

Catalytically Reformed Landfill Gas





Significantly Reduced Emissions for Catalytically Processed LFG

2 kW_e Laboratory test engine

CH_3Cl on Catalytic Rxns

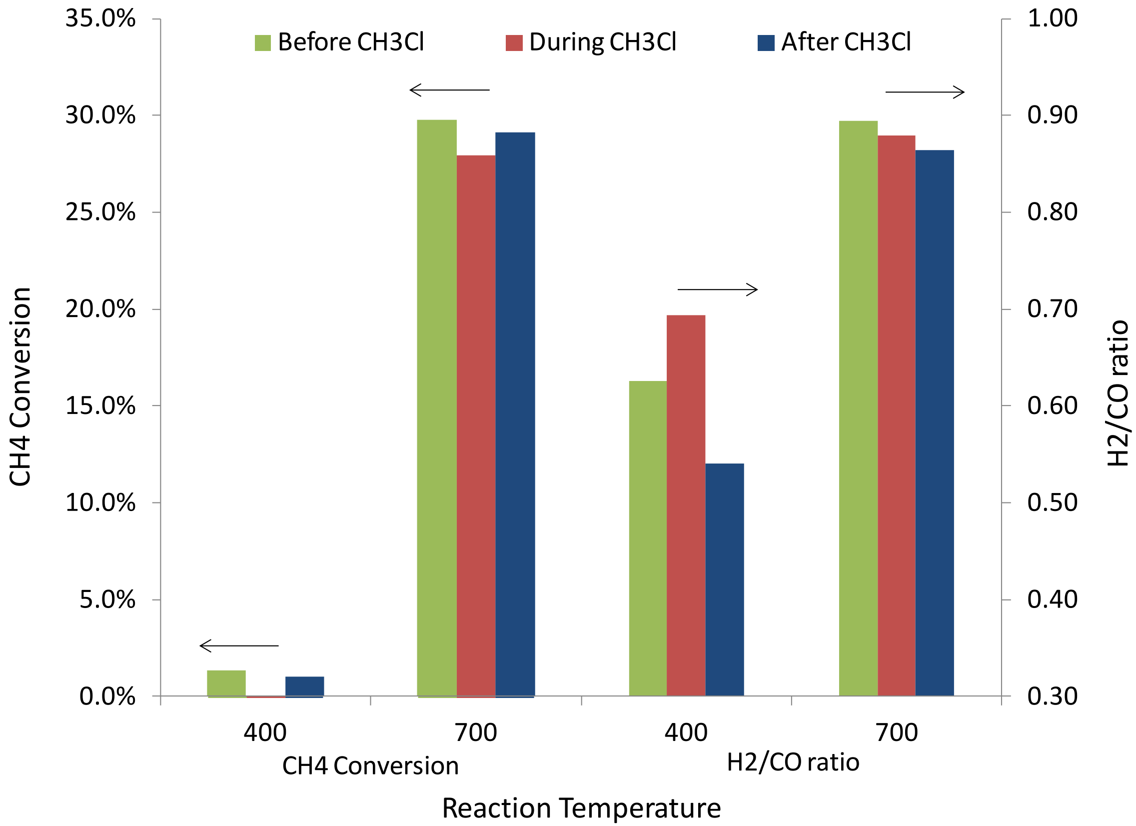
•CH_3Cl reduces methane conversion activity while on stream

•After CH_3Cl is turned off, some activity returns

•CH_3Cl also affects H_2/CO ratio of product stream, indicating change in selectivity

Combination of reversible and irreversible poisoning occurring

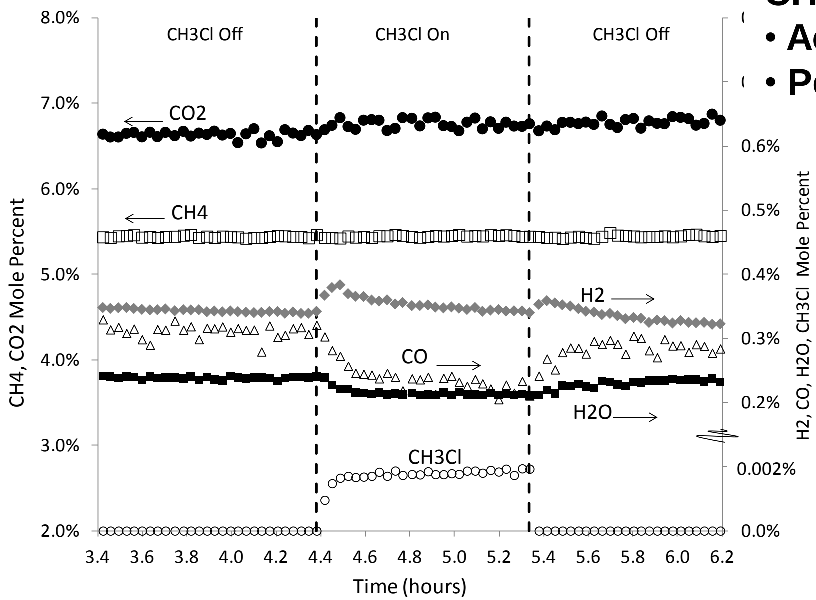
- **•Irreversible: Coking?**
- **•Reversible: Cl deposition?**

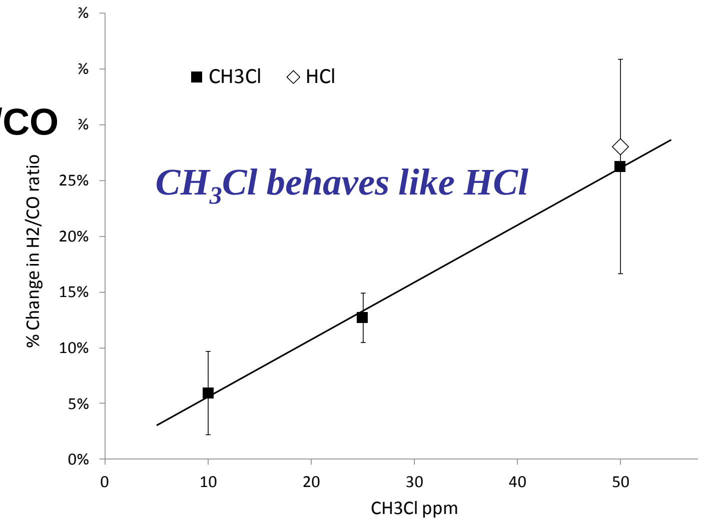


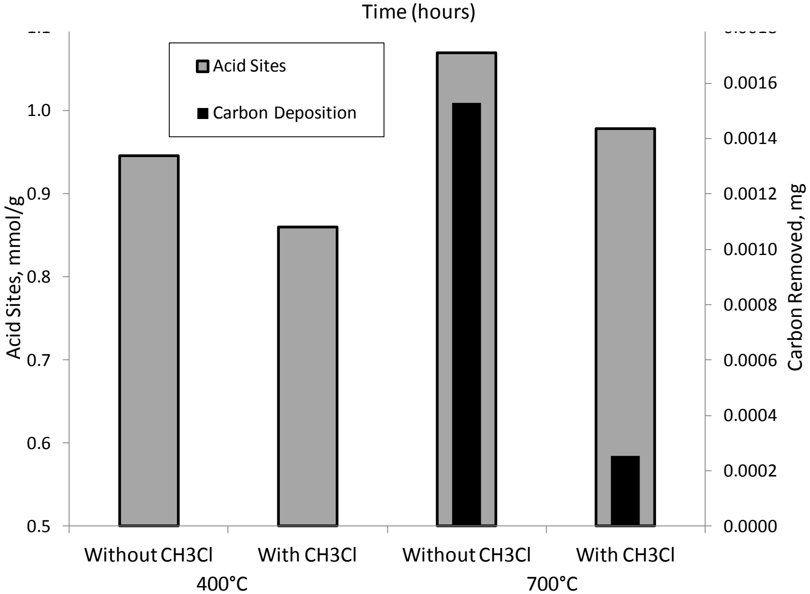
CH_4=5% CO_2=5% CH_3Cl=0.005% (50 ppm)
4% Rh/Al_2O_3, powder
GHSV=700,000 hr^{-1}

LFG Impurity Impacts

CH_3Cl injection to feed
- **Activity maintained**
- **Percent change in H_2/CO**



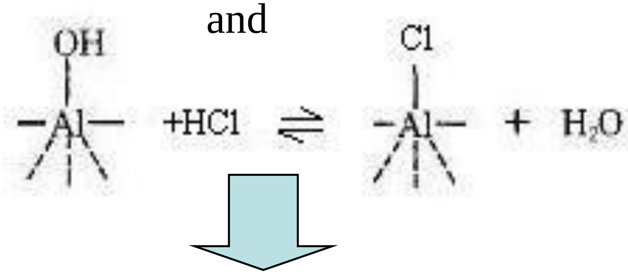




(1) $CH_3Cl + H_2O \rightarrow 2H_2 + CO + HCl$

and

(2)

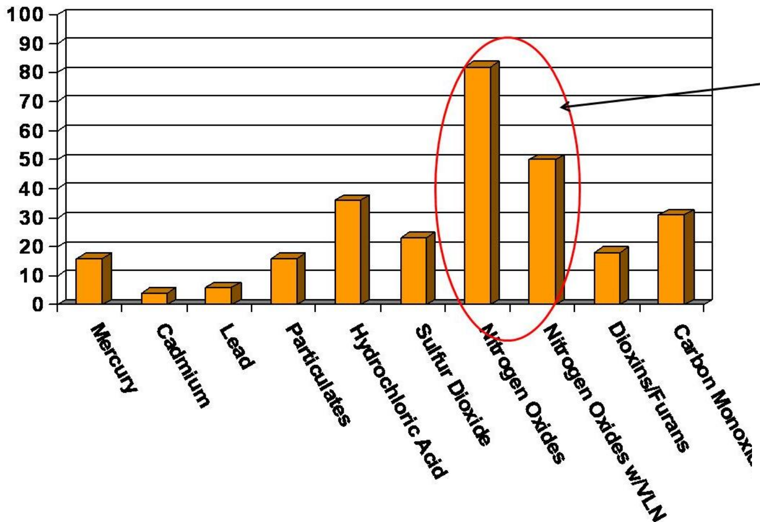


$CO + H_2O \rightarrow H_2 + CO$

- ***Cl forms an Al-Cl entity on the surface impacting the reactions producingH_2***
- ***Cl reversibly impacts activity & H2O helps***

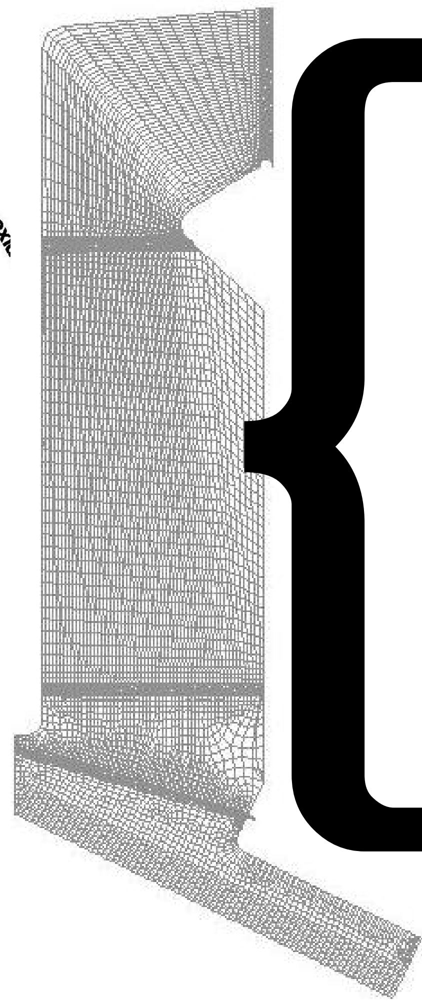
Detailed Chemical Kinetic Mechanism: NOx

Covanta WTE Emission as % of MACT Limits



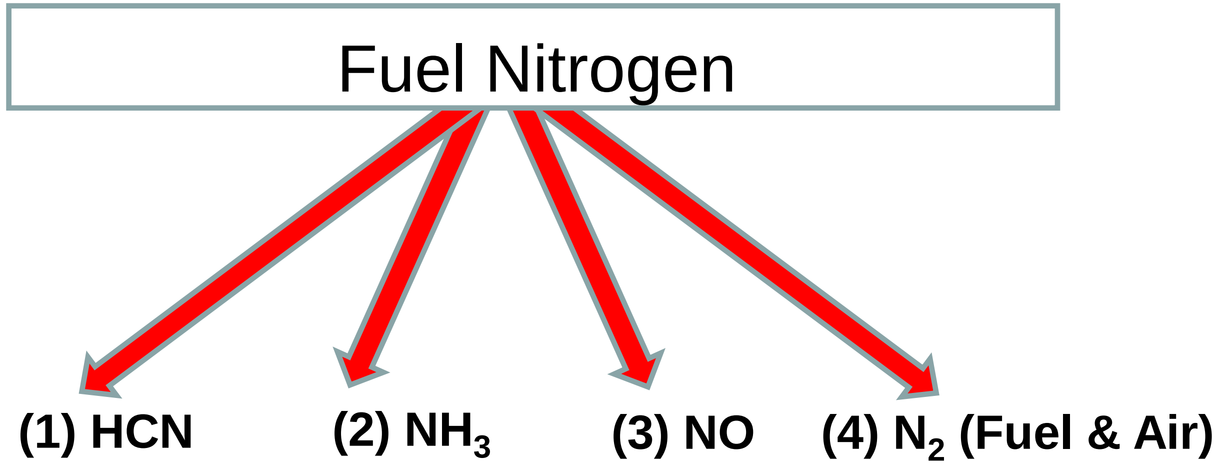
GRI 3.0*-309 reaction step DCKM contains 50 species and is used in conjunction with Eddy Dissipation Concept Model for turbulent-chemistry reaction in the boiler.

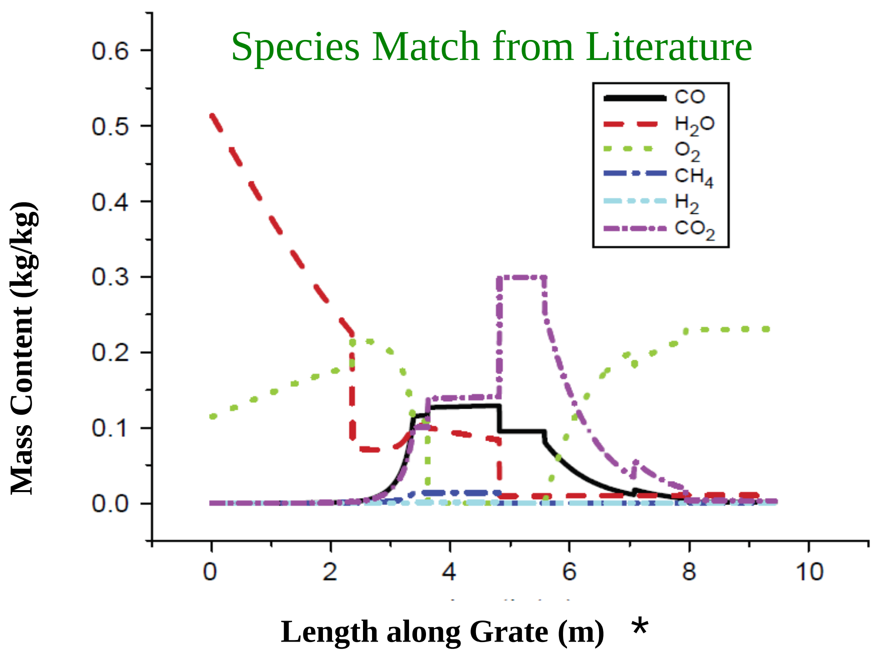
- 3-D CFD to understand flow characteristics of chemical species in WTE boilers
- Inlet boundary condition to CFD model is "***above bed***" gas phase
- Solid phase not modeled
- (DCKM) to predict combustion products

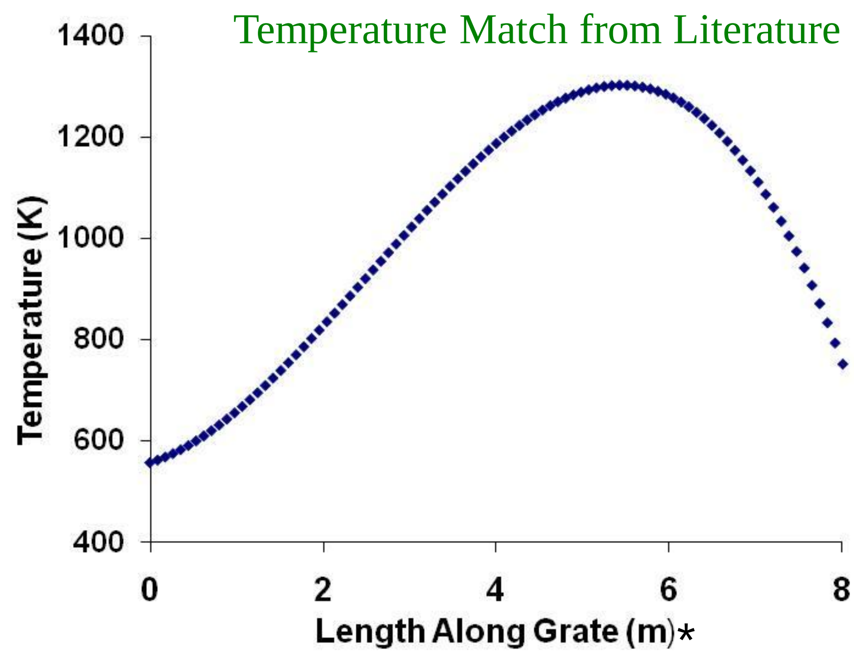


```
REACTIONS
2O+M<=>O2+M                              1.200E+17   -1.000        .00
H2/ 2.40/ H2O/15.40/ CH4/ 2.00/ CO/ 1.75/ CO2/ 3.60/ C2H6/ 3.00/ AR/  .83/
O+H+M<=>OH+M                             5.000E+17   -1.000        .00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
O+H2<=>H+OH                              3.870E+04    2.700    6260.00
O+HO2<=>OH+O2                            2.000E+13     .000        .00
O+H2O2<=>OH+HO2                          9.630E+06    2.000    4000.00
O+CH<=>H+CO                              5.700E+13     .000        .00
O+CH2<=>H+HCO                            8.000E+13     .000        .00
O+CH2(S)<=>H2+CO                         1.500E+13     .000        .00
O+CH2(S)<=>H+HCO                         1.500E+13     .000        .00
O+CH3<=>H+CH2O                           5.060E+13     .000        .00
O+CH4<=>OH+CH3                           1.020E+09    1.500    8600.00
O+CO(+M)<=>CO2(+M)                       1.800E+10     .000    2385.00
   LOW/ 6.020E+14      .000    3000.00/
H2/2.00/ O2/6.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/3.50/ C2H6/3.00/ AR/ .50/
O+HCO<=>OH+CO                            3.000E+13     .000        .00
O+HCO<=>H+CO2                            3.000E+13     .000        .00
O+CH2O<=>OH+HCO                          3.900E+13     .000    3540.00
O+CH2OH<=>OH+CH2O                        1.000E+13     .000        .00
O+CH3O<=>OH+CH2O                         1.000E+13     .000        .00
O+CH3OH<=>OH+CH2OH                       3.880E+05    2.500    3100.00
O+CH3OH<=>OH+CH3O                        1.300E+05    2.500    5000.00
O+C2H<=>CH+CO                            5.000E+13     .000        .00
O+C2H2<=>H+HCCO                          1.350E+07    2.000    1900.00
O+C2H2<=>OH+C2H                          4.600E+19   -1.410   28950.00
O+C2H2<=>CO+CH2                          6.940E+06    2.000    1900.00
O+C2H3<=>H+CH2CO                         3.000E+13     .000        .00
O+C2H4<=>CH3+HCO                         1.250E+07    1.830     220.00
O+C2H5<=>CH3+CH2O                        2.240E+13     .000        .00
O+C2H6<=>OH+C2H5                         8.980E+07    1.920    5690.00
O+HCCO<=>H+2CO                           1.000E+14     .000        .00
O+CH2CO<=>OH+HCCO                        1.000E+13     .000    8000.00
O+CH2CO<=>CH2+CO2                        1.750E+12     .000    1350.00
O2+CO<=>O+CO2                            2.500E+12     .000   47800.00
O2+CH2O<=>HO2+HCO                        1.000E+14     .000   40000.00
H+O2+M<=>HO2+M                           2.800E+18    -.860        .00
O2/ .00/ H2O/ .00/ CO/ .75/ CO2/1.50/ C2H6/1.50/ N2/ .00/ AR/ .00/
H+2O2<=>HO2+O2                           2.080E+19   -1.240        .00
H+O2+H2O<=>HO2+H2O                       11.26E+18    -.760        .00
H+O2+N2<=>HO2+N2                         2.600E+19   -1.240        .00
H+O2+AR<=>HO2+AR                         7.000E+17    -.800        .00
H+O2<=>O+OH                              2.650E+16    -.6707  17041.00
2H+M<=>H2+M                              1.000E+18   -1.000        .00
H2/ .00/ H2O/ .00/ CH4/2.00/ CO2/ .00/ C2H6/3.00/ AR/ .63/
2H+H2<=>2H2                              9.000E+16    -.600        .00
2H+H2O<=>H2+H2O                          6.000E+19   -1.250        .00
2H+CO2<=>H2+CO2                          5.500E+20   -2.000        .00
H+OH+M<=>H2O+M                           2.200E+22   -2.000        .00
H2/ .73/ H2O/3.65/ CH4/2.00/ C2H6/3.00/ AR/ .38/
H+HO2<=>O+H2O                            3.970E+12     .000     671.00
H+HO2<=>O2+H2                            4.480E+13     .000    1068.00
```

Inlet Boundary Conditions Developed







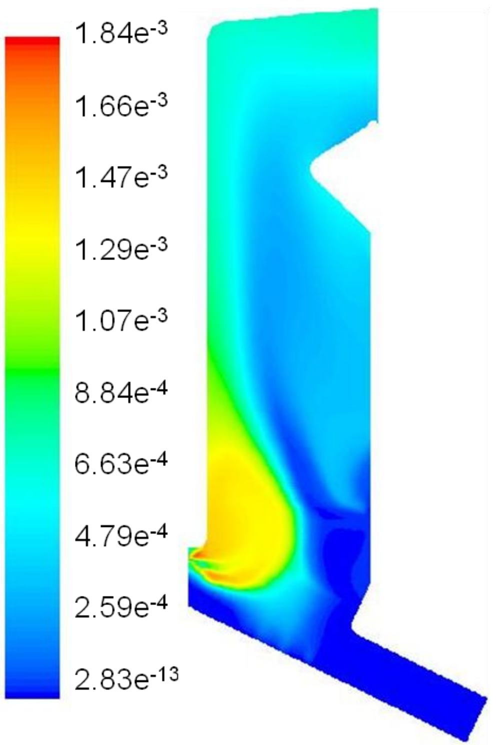
* Huai, X.L., et al, Chemical Engineering Science. 63 (2008), 3100-3113.

- ***Above-grate inlet conditions developed from published literature***
- ***Fuel nitrogen directed to 4 possibilities***

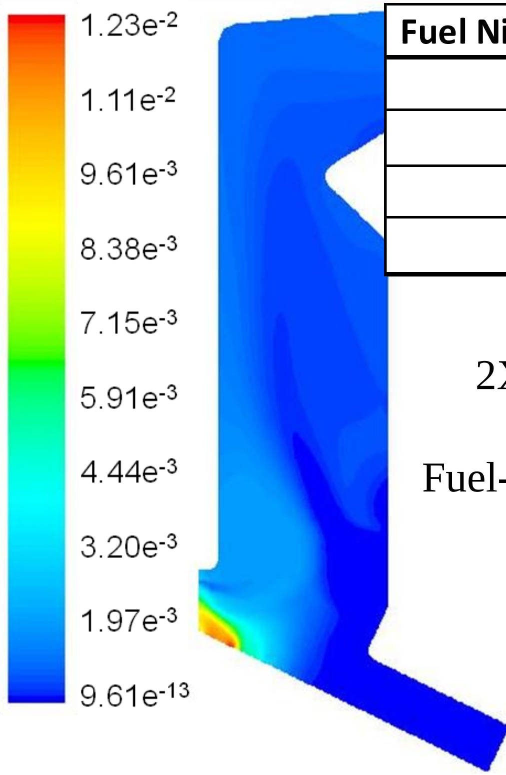
Model Results-DCKM NOx

Contours of NO (mol/mol)

Fuel-N →(1)HCN or (2)NH_3



Fuel-N →(3)NO

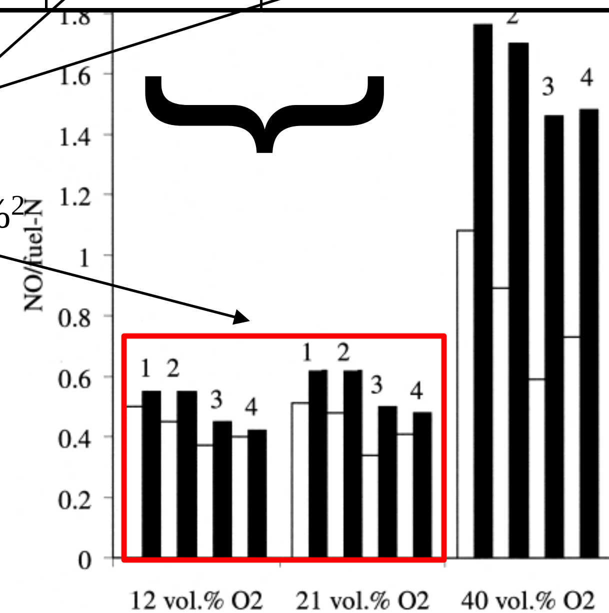


Model Results for Precursors

Fuel Nitrogen Conversion	NO (ppmdv)	Expected NO (ppmdv)
HCN	993	400[1]
NH_3	957	
NO	1036	
N_2	10	

2X difference

Fuel-N → NO ~50%[2]



Fuel – N to HCN or NH_3 precursor: NOx formation at 2° air inlet
Fuel – N to NO precursor: little change in boiler
Likely Fuel – N to NO direct conversion is ~50%

1.White, M., et al., New Process for Achieving Very Low NOx2009. NAWTEC17-2372.
2. Sorum,L., et al., Formation of NO from Combustion of Volatiles from Municipal Solid Waste, Comb Flame ,123 p.195

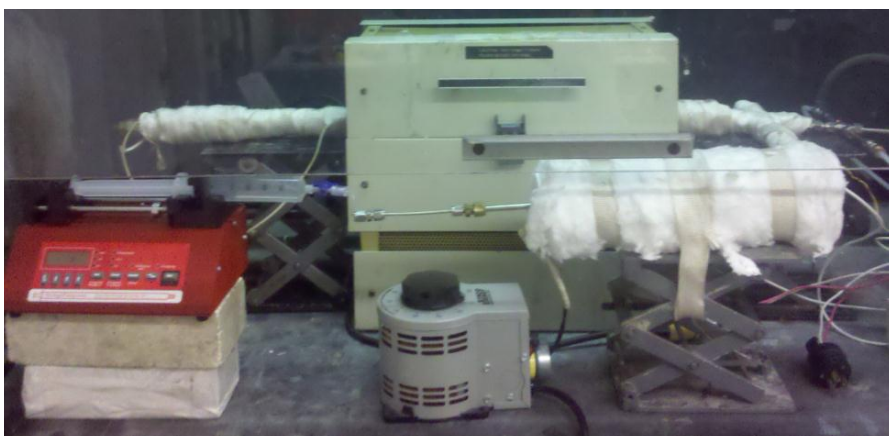
Experimental Setup: Corrosion

Experimental approach: determine whether corrosion is decreased by converting deposited chloride salts with higher SO_2:HCl

Steel	C	Si	Mn	P	S	Ni	Cr	Mo	Fe	Nb+Ta	Cu	Al	Ca	N	Ti	V	W	B
NSSER-4	0.04	2.5	0.8	-	-	13.1	17.3	2.5	bal.	-	-	-	-	-	-	-	-	-

Coupon Dimensions: 0.5” x 1.0” x 0.1”

NSSR: Type of Stainless Steel
SA178A: low alloy carbon steel

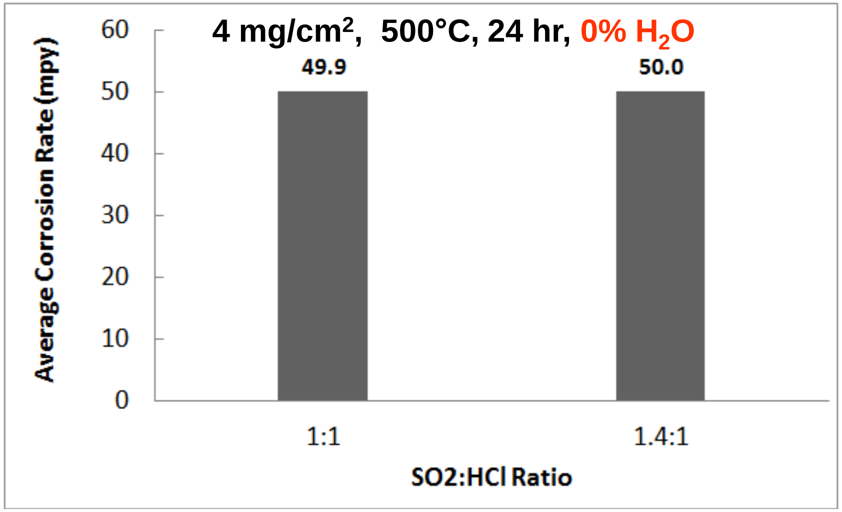


Flow through reactor for isothermal testing

Testing Conditions	
Temperature	425-500°C
Time	50
Total Flowrate	500 cm^3/min (STP)
Gas Concentrations	
HCl	800 ppmv
SO_2	100-500 ppmv
H_2O	0-15%
O_2	8%
CO_2	12%
N_2	Balance

SO2:HCl and relationship w/ corrosion

No water present during test – no effect of sulfur

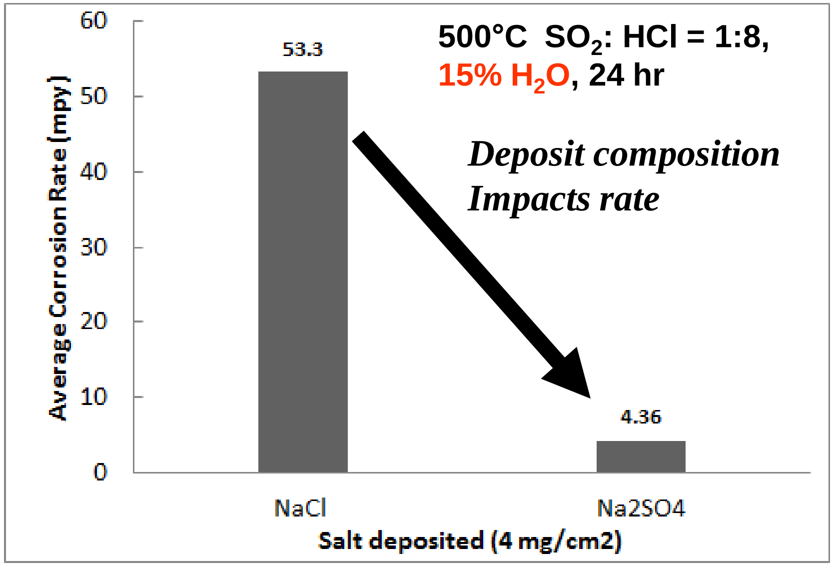


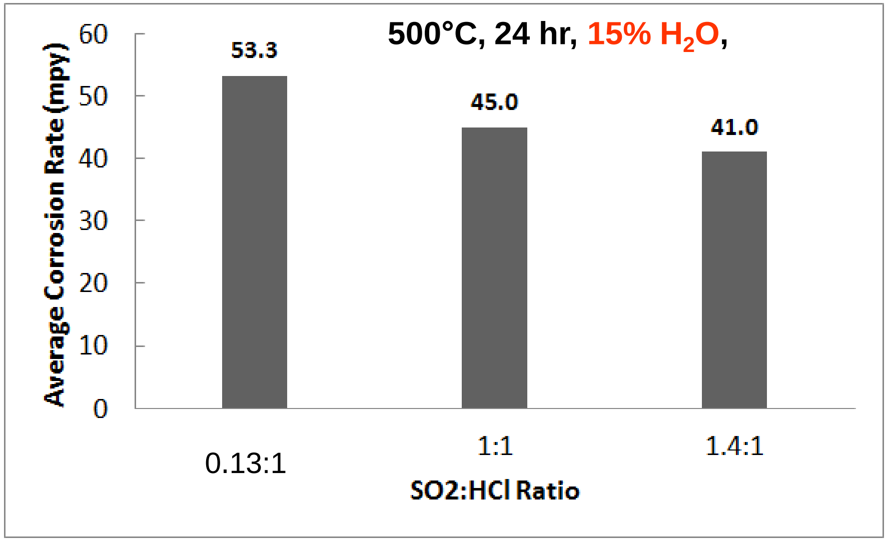
Water present will convert NaCl → Na_2SO_4

Likely reaction

$2NaCl_{(s)} + 0.5\ O_{2\,(g)} + SO_{2\,(g)} + H_2O_{(g)}$
$\rightarrow Na_2SO_{4\,(s)} + 2HCl_{(g)}$

T (°C)	ΔG (kJ/mol)
200	-136
300	-121
400	-108
500	-95
600	-83





23% reduction observed from 0.13 → 1.4 SO_2 increase

Consistent with literature (*Krause, H.H.,Paper No. 242, CORROSION/91, NACE (1991)*)

Ash/Char as a Catalyst: Added Value

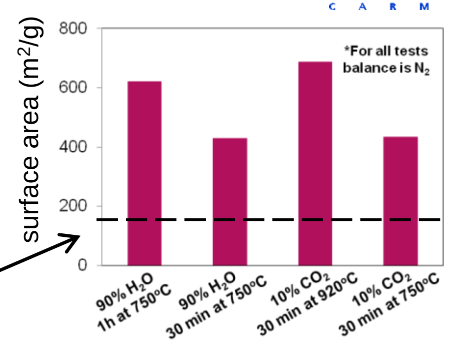
Combustion & Catalysis Laboratory

Waste-To-Energy Research and Technology Council

ECOLE DES MINES D'ALBI CARMAUX

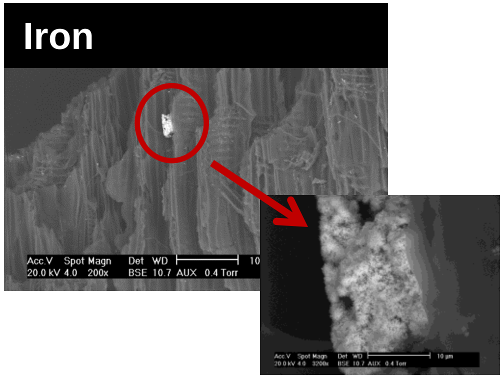
The fate of ash/char:
- landfill or ashfill
- used in construction applications
- metals recovery (ash)
- catalytic applications (e.g. NOx abatement)

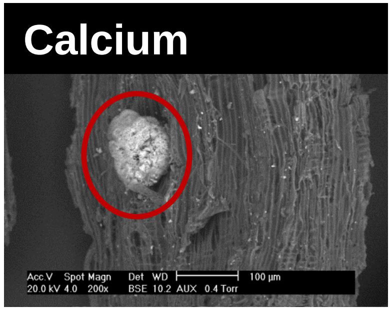
surface area > conventional catalysts



SA for γ-Al_2O_3

Catalytic metals and minerals
are present in Ash/char



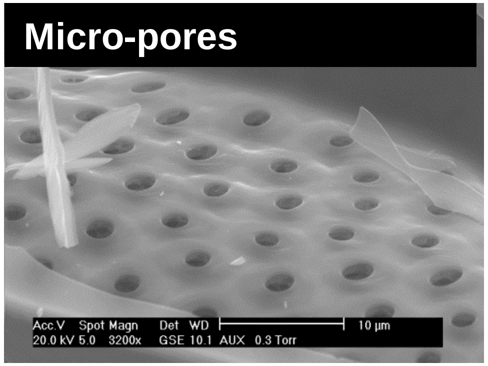


Metals (Fe, etc) are used in catalytic applications
→enhances catalyst performance

Other metals & minerals measured in char: Mg, K, Na

High Surface Area: increases available catalyst sites

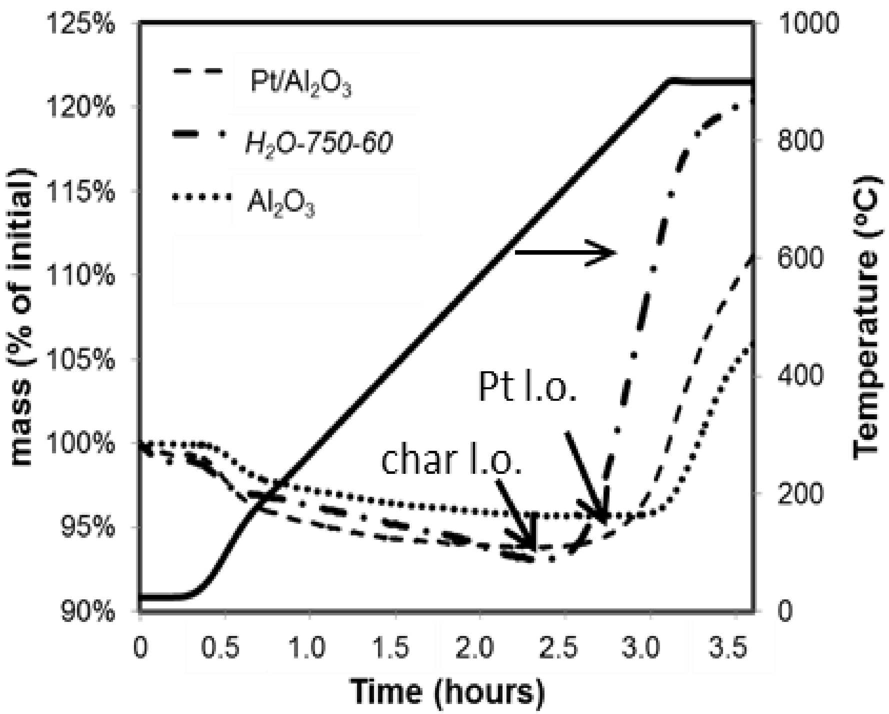
Ash/char contains micro- and nano-pores



the City College of New York

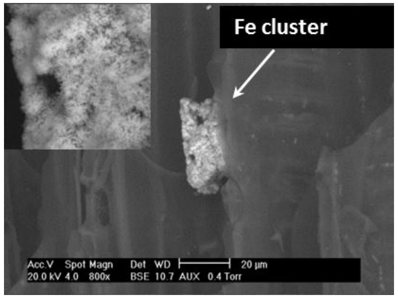
Comparison to conventional catalysts

- Ash/Char was compared to commercial Pt/Al_2O_3 catalyst and to Alumina (no cat)
- Reaction for comparing catalysts: $CH_4 \rightarrow C + H_2$

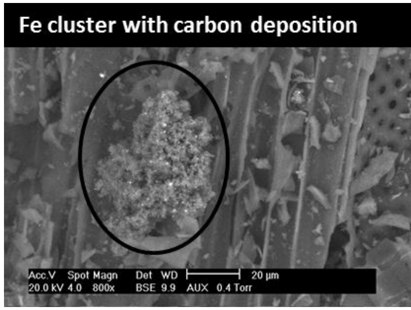


<u>Light off temperature</u>:
Ash/char – 675°C
Pt/Al_2O_3 – 775°C
Al_2O_3 – 850°C

Pre-test ash/char



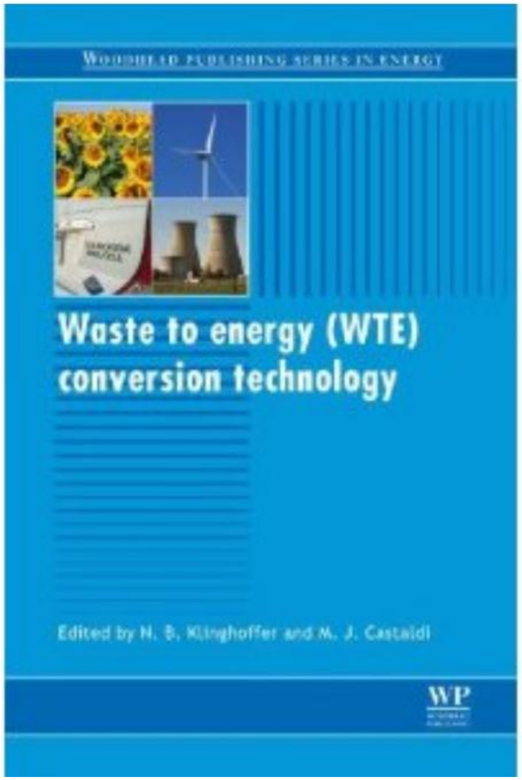
Post-test ash/char



Lower temperature activity compared to commercial catalyst

Post-test results:
<u>Carbon buildup on catalyst</u>
→Iron may be an active site
→Carbon-metal interactions may enhance activity

General Activities



Editors: Naomi Klinghoffer and Marco J Castaldi
•13 Chapters covering technologies to policies
•Woodhead Publishers
•On Sale Now!

WTE developing countries

Nigeria – Regulations & $$

LAWMA
New Trend in Efficiency & Professionalism

Bulgaria – Follows EU regulations, issue is $$

International Visitor Leadership Program" (IVLP)

Brings "up-and-coming" young leaders from other countries to the U.S. to learn from American counterparts

Ms. Milena Bozhanova IVANOVA
Deputy Mayor, Municipality of Popovo
Mr. Georgi KENOV
Mayor of Sungurlare
Mr. Rozalin Petkov PETKOV
Deputy Mayor of Plovdiv Municipality
Mr. Dimitar Zhivkov STOYKOV
Mayor of Pleven Municipality

Expanding WTERT

Combustion & Catalysis Laboratory

WTERT Waste-To-Energy Research and Technology Council

The City College of New York

Named one of *Princeton Review's* **Best Colleges** of 2013 | The City College of New York

Student Research

- Jeff LeBlanc, PhD Candidate, ChE
  - Gasification

Sustainability in Urban Environment

- Capstone project (Engineering, Science & Architecture)

  "An Integrated Waste-to-Energy Plan for New York City"
- Waste to Energy Course (Spring 2013, proposed)
- Executive Committee Member

the City College of New York

Acknowledgments

- **Students**
  - Dr. McKenzie Kohn (LFGTE Catalyst Testing – **Poster**)
  - Marcella Lusardi (LFGTE Engine Testing – **Poster**)
  - Alex Frank (WTE Modeling)
  - Tim Sharobem (Corrosion – **Poster**)
  - Naomi Klinghoffer (Beneficial Use of Ash **- Poster**)
  - Alexsandra Guerra
- **Visiting Students**
  - Lu Liang (Yoshikawa/TokyoTech)
  - Mi Yan (Cen,Li/Zhejiang)

You, the audience for listening

Az testimony
WTE book
CCNY Sustainability course
Washington GBB
NYIT WTE symposium
WasteEng
IWWG
Veolia – thermal deg IWWG
IT3/ASME/WTERT
Technical due diligences – gasification
Satellite media tour