

# Halogenated Sorbents for Mercury Control



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**Panel Discussion**

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# Halogenated Sorbents

## Introduction

- **Excellent Results for Mercury Capture**
- **Large-Scale**
- **Bromine - Promoted Carbons**
- **Chlorine - Treated Carbons**
- **Other Work on Iodine – Promoted Carbons**

# Halogen-Treated Activated Carbons

## Earlier Work

- 1971 Matsumura: I-AC
- 1993 Quimby: Cl-AC
- 1994 Livengood: Halogen salts-AC
- 2000 NETL In-house: HCl-AC, Cl<sub>2</sub>-AC, I<sub>2</sub>-KI-AC

Recommend use of inexpensive chlorine-promoted carbons

- 2001 NETL In-house: Thief Sorbents can be treated with halogens, if desired



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# Technical Challenges

## Environmental Issues

- Off-Gassing of Halogen:  $I_2$  Volatile
- Leaching of Halogen
- Undesired Side-Products: Flue Gas Halides

## Corrosion Issues

- Halogens & Compounds Corrosive
- $SO_3$  is Corrosive

## Impacts on Fly Ash

- Salability for Concrete



# Sorbents are Catalysts

## Flue Gas is a Complex Mixture

- **Carbons & Metals are Catalysts**

### Formation of Flue Gas Halides:

- Carbonyl halides  $\text{CO}_{(\text{ad})} + \text{X}(\text{ad}) \rightarrow \text{COX}$
- Sulfuryl halides  $\text{SO}_{2(\text{ad})} + 2 \text{X}(\text{ad}) \rightarrow \text{SO}_2\text{X}_2$
- Nitrosyl halides  $\text{NO}_{(\text{ad})} + \text{X}(\text{ad}) \rightarrow \text{NOX}$
- Sulfur trioxide  $\text{SO}_{2(\text{ad})} + \text{O}(\text{ad}) \rightarrow \text{SO}_3$
- Where X is Cl or Br
- **Must always look out for undesired side effects**

# Carbon Sorbents are Catalysts

## Phosgene Formation

### Activated Carbon is a Catalyst

- **Commercial Catalyst for Phosgene**
- **$\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$**
- **Unlikely to be a problem for regular ACI and combustion modification**
- **Cl-treated AC should be even better catalyst**

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# Phosgene

- **AC Catalyst at Flue Gas Temperatures**
- **Cl-AC Excellent Catalyst**
- **Five Billion Pounds Manufactured Annually**
- **Important for Plastics & Pharmaceuticals**
- **Highly Toxic**
- **Permissible Exposure Limit: 0.1 ppm**



# Brominated Activated Carbons

## Carbonyl Bromide

- $\text{COBr}_2$
- $\text{CO} + \text{Br}_2 \rightarrow \text{COBr}_2$
- Highly Toxic
- Br-Treated AC Excellent Catalyst

# Stability of Flue Gas Halides

- **COX, SO<sub>2</sub>X<sub>2</sub>, and NOX**
- **Reactant concentrations exceedingly low**
- **Contact times small for ESP**
- **Rapid hydrolysis**
- **Will form, but not persist in flue gas**

# Crude Halogen Mass Balance

- 48 tons mercury per year
- Sorbent: 1 - 10% by weight halogen
- ACI upstream of ESP
- 10,000: 1 sorbent:mercury mass ratio
- 5,000 – 50,000 tons halogen per year
- Within fly ash & flue gas streams
- Upper limit assuming wide application
- Is additional 5 – 50 thousand tons halogen entering environment annually significant ?

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# Incinerator Flue Gas

- **Example for Utility Industry**
- **Regulated for Mercury Emissions**
- **High Chlorine Concentration in Flue Gas**
- **Application of ACI**
- **Impacts**
- **Corrosion**
- **Fly ash**
- **Leaching**
- **Off-Gassing**

## Issues to be Resolved

- Flue Gas Halides Unlikely to be a Problem
- COX, SO<sub>2</sub>X<sub>2</sub>, and NOX Hydrolyze Rapidly
- Corrosion Unlikely to be Major Issue
- Existing Incinerator Flue Gas Examples

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- Halogen Introduction into Environment
- Fly Ash Solubility
- May Cause Concern
- More Research Suggested

