



# **Analysis of Wet FGD Wastewaters**

## ***overcoming matrix interferences and complying with discharge regulations for metals***

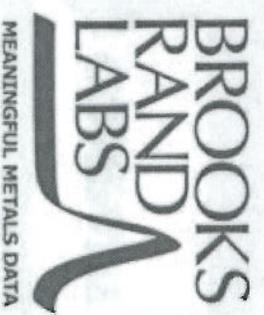
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**Brooks Rand Labs**



Presented June 16, 2011  
McIlvaine Company "Hot Topics Hour" Webinar Series

# Background



## 2010 Effluent Limitation Guidelines (ELGs)

- EPA to revise standards for metals in water discharges from power plants
- Primary focus on coal-fired power plants:
  - Generate most of the pollutant loads
  - Coal dominates forecasted future power generation

## Key Waste Streams

- The **FGD** wastewater from new SO<sub>2</sub> controls
- Ash pond discharges

# Current Status of ELGs



Detailed and comprehensive study 2007-2009

- Data collection included
  - Questionnaire (9 different companies)
  - Wastewater sampling & split study by UWAG
  - Site visits

Primary metals of concern for Env. & HH Risk

Mercury (Hg)

Selenium (Se)

Arsenic (As)

EPA: Unregulated toxic metals are present,  
but CAN be reduced

# Success of Treatment Technologies Depends on

## Accurate Data

Assumption:

EPA Method + Accredited Lab = Accurate Data

# NOT ALWAYS TRUE

# FGD Waters are Complex and Variable



Total suspended solids	< 10 mg/L – 17%
Total dissolved solids	4000 – 68,000 mg/L
pH	4.5 - 9
Sulfate	450 – 22,000 mg/L
Chloride	1,000 – 28,000 mg/L
Calcium	600 – 5,700 mg/L
Magnesium	400 – 7,700 mg/L
Sodium	20 – 4,800 mg/L
Total organic carbon	5 – 1100 mg/L

# Risk of Inaccurate Data due to Matrix Interferences



What is an Interference?

Common Interferences in FGD Waters:

- Physical (e.g., high levels of solids)
- Spectral (due to analytical method)

Mass spectral **polyatomic interferences** with  
EPA Method 200.8 (ICP-MS)

# Analytical Interference

## Example



Arsenic (*As*) - only one isotope at mass 75

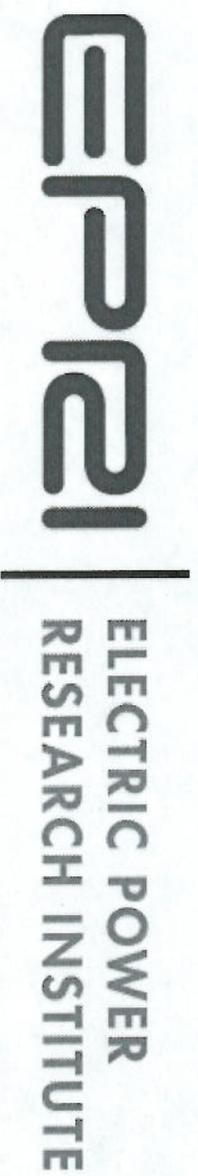
- major interference:  $^{40}\text{Ar}^{35}\text{Cl}^+$  = mass 75

Similar polyatomic interferences for Se, Cr,  
and other metals

# Overcoming Interferences



- Specialty methods can be used
  - Developed with support from EPRRI
  - Modification of EPA 200.8 for ICP-MS
- Specialty trace metals labs can be utilized
  - Cutting-edge instrumentation and methods
  - Analysts with advanced analytical chemistry skills



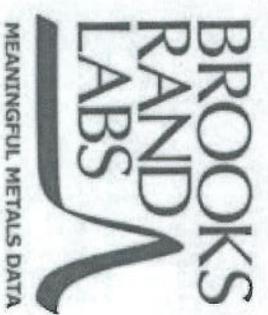
EPRI Technical Update Report #1017978 (2009):

“Trace Metals Determination in Flue Gas  
Desulfurization Waters: Optimization of  
Dynamic Reaction Cell ICP-MS”

Principal Investigator: M. Briscoe, Brooks Rand Labs

EPRI Project Manager: N. Goodman

**More accurate data for:  
As, Cd, Cr, Cu, Fe, Ni, Sb, Se, V, and Zn**



# Arsenic Interferences

90-99% of reported concentration can be due to an INTERFERENCE

Actual FGD Wastewater Treatment System Effluent Data:

Site ID	Regular ICP-MS	DRC Method
1	26	2
2	510	18
3	110	11
4	3200	21

All results are in units of ppb or µg/L

# Chromium Interferences

97-99% of reported concentration can be due to an **INTERFERENCE**

Actual FGD Wastewater Treatment System **Effluent** Data:

Site ID	Regular ICP-MS	DRC Method
1	30.6	< 0.23
2	267	2.73
3	222	< 1.2
4	96.8	3.37

All results are in units of ppb or µg/L

# Selenium Interferences

20-55% of reported concentration can be  
due to an **INTERFERENCE**

Actual FGD Wastewater Treatment System **Effluent** Data:

Site ID	Regular ICP-MS	DRC Method
1	151	102
2	6740	5460
3	750	504
4	14100	6220

All results are in units of ppb or µg/L

# Validation of DRC Method

## Selenium

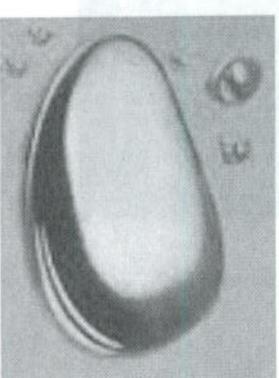
Site ID	DRC Method	HR-ICP-MS
1	102	115
2	5460	5580
3	504	550
4	6220	6270

All results are in units of ppb or µg/L

# And What About Mercury?

- Method 1631
  - Cold Vapor Atomic Fluorescence
  - Detection Limit = 0.15 ng/L
- Watch out for Suppression
  - Matrix Spikes
  - Analysis at Multiple Dilutions

**Hg**

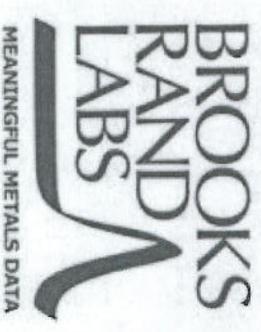


## In Conclusion...



- New Regulations for FGD Wastewaters
- FGD Wastewaters are Complex
  - Bias due to Interferences is a RISK
- Accurate data is achievable
  - Careful selection of method

# Metals Speciation in FGD WW



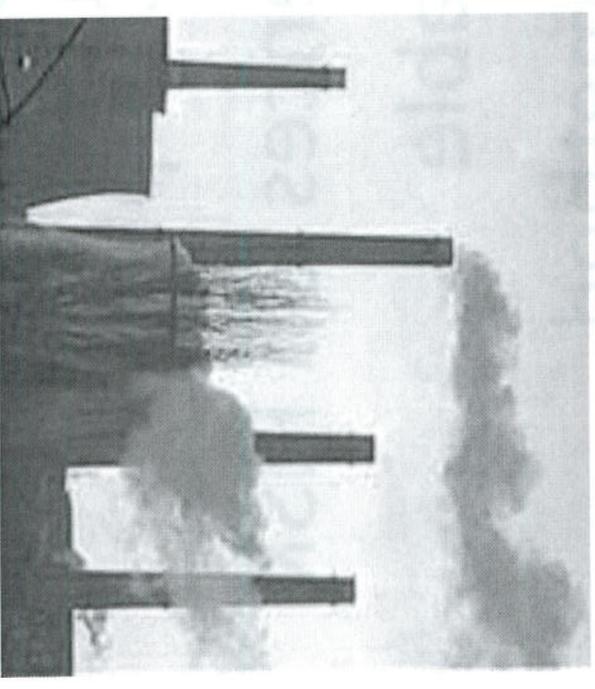
Selenium: Se(IV), Se(VI),

SeCN, SeSO<sub>3</sub>, others

Arsenic : As(III), As(V),

MMAs, DMAs, others

Mercury: MeHg, Hg(II), Hg<sup>0</sup>



# Thank you!

## Questions?

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