Specialized Analyses of

Flue Gas Desulfurization Wastewater

for Heavy Metals







As was recently announced, the US EPA intends to significantly revise wastewater effluent limit guidelines for discharge permits granted to coal-fired power plants. The current rule (40 CFR Part 423) was promulgated in 1982, and the EPA has determined that it has not kept pace with changes in the industry over the past several decades.

The volume and composition of wastewater created by coal-fired power plants has changed dramatically with the installation and operation of modern air pollution control systems. In order to meet individual state regulations and air quality standards set by the US EPA, coal-fired power plants are required to remove sulfur dioxide emissions from the flue gas they generate. Over 85% of flue gas desulfurization (FGD) systems use wet scrubbers that employ a limestone-forced-oxidation process, spraying slurry over flue gas to convert gaseous sulfur dioxide to calcium sulfate particulates. Once the level of suspended solids in the slurry reaches a certain limit, it is purged from the scrubber for dewatering to separate the calcium sulfate, or gypsum, from the purge water.



Typical FGD Wastewater Lifecycle

EXAMPLE WASTEWATER COMPOSITION

рН	4.5 - 9
total suspended solids	<10 mg/L - 17%
total dissolved solids	4000 - 68,000 mg/L
total orgainic carbon	5 - 1100 mg/L
sulfate	4500 - 22,000 mg/L
chloride	1000 - 28,000 mg/L
calcium	600 - 5700 mg/L
magnesium	400 - 7700 mg/L
sodium	20 - 4800 ma/L

While this process removes harmful pollutants from the air and creates gypsum as a valuable byproduct, the resultant wastewater is unique even among industrial wastewater streams.

In addition to elevated temperatures and levels of suspended and dissolved solids, FGD wastewater can have extremely elevated concentrations of chloride, carbon, sulfur, bromine, and alkali earth metals (sodium, calcium, potassium, magnesium).

Various treatment processes, such as the addition of alkali, organosulfide, ferric chloride, or hydrochloric acid, which can aid in the removal of specific heavy metals while hindering the removal of others, further complicates the accurate characterization of the matrix.

the accurate characterization of the matrix. The unusual and constantly shifting composition of FGD wastewater presents circumstances that would otherwise rarely be encountered in analyzing wastewater samples and presents issues that many laboratories are not capable of recognizing or resolving. Brooks Rand Labs, in close cooperation with representatives of the electric utilities, university research groups, and environmental engineering firms, has conducted extensive research and investigation to develop specialized and reliable analytical methods/ techniques for the determination of many trace metals in FGD wastewater that overcome the matrix-associated

Standard analytical methods for the determination of trace metals in FGD wastewater, such as ICP-MS by EPA Method 200.8 or EPA Method 6020, are often extremely prone to mass spectral interferences brought on by the presence and concentrations of the constituents noted above.

Such interferences can lead to results that may be biased high by as much as two orders of magnitude for metals such as arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), selenium (Se), vanadium (V), and zinc (Zn).

Without an analytical technique to eliminate the interferences that lead to elevated results, decision makers might be acting on inaccurate data.

Inaccurate data, like that produced for many analytes that are affected by polyatomic interferences when analyzed by standard ICP-MS, can lead to confusion about the actual concentration of trace metals in FGD wastewater and the effectiveness of various treatment techniques, investigation or implementation of unnecessary treatment technologies, and costly delays.

Comparisons of results derived from analyses of FGD wastewater samples by standard ICP-MS with those from the significantly more accurate, precise, and expensive sector-field, or high-resolution, ICP-MS (HR-ICP-MS) method demonstrate how significantly these interferences can affect the quality of data when no actions have been implemented to mitigate them.

interferences without incurring the prohibitive costs of HR-ICP-MS.

Analysis by ICP-MS – when coupled with Dynamic Reaction Cell[™] (DRC) technology, an advanced chemical resolution system optimized with the appropriate reaction gasses – can eliminate many of the mass spectral interferences associated with the analysis of FGD wastewater, producing accurate data and at a fraction of the cost of analysis by HR-ICP-MS.

At Brooks Rand Labs, these specialty methods are tailored to the specific characteristics of the wastewater from each power plant.

Example Results by Analytical Methods (µg/L)

Analyte	Standard ICP-IVIS	HR-ICP-MS	ICP-DRC-MS
As	3210	11	13
Cr	267	3.2	3.1
Cu	56	18	18
Ni	175	130	135
Se	14100	6270	6220
V	131	50	49
Zn	4840	4600	4640

To learn more about the innovative analytical methods Brooks Rand Labs has developed to accurately assess the concentrations of trace metals in FGD wastewater, contact us today.

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Under the EPA Clean Air Interstate Rule, the first phase of mercury reductions from coalfired power plants mainly results as a co-benefit of reducing other pollutants with existing control technologies. Nearly 35% of the mercury that currently goes into US coal-fired power plants is captured by air pollution control systems, whose key functions are typically to trap particulates or sulfur emitted with flue gasses. However, the mercury that is captured by FGD systems tends to persist in a highly volatile form due to the composition of the wastewater and can prove difficult to properly collect and analyze.

As one of the preeminent commercial laboratories in mercury analysis and research, Brooks Rand Labs provides electrical utilities with comprehensive services for the accurate determination of mercury in nearly every form. We routinely analyze coal, fly ash, ambient air, flue gas, wastewater, and byproducts for mercury, specific forms of mercury compounds and their mobility. Below are just some of the mercury analyses we offer for aqueous or solid matrices. For more information, contact a BRL representative today.

- total/low-level mercury
- inorganic mercury
- methylmercury
- extractable organic mercury
- semi-mobile mercury
- water soluble mercury
- organo complexed mercury
- mineral bound mercury

volatile/elemental mercury
acid labile mercury
dimethylmercury
extractable inorganic mercury
non-mobile mercury
weak acid soluble mercury
strong complexed mercury
cinnabar



Compliance with wastewater discharge permit regulations for metals is typically accomplished by the implementation of sophisticated and multi-staged treatment processes, the ultimate effectiveness of which is demonstrated by the measurement of "total recoverable" concentrations. However, the efficiency of many individual treatment processes is highly dependent upon the specific characteristics of the metals of concern.

The determination and quantitation of volatile, organic, and inorganic fractions, as well as specific organometallic compounds or elemental electron valence states is often described as the analytical practice of "speciation."

Particular species often react more or less effectively to specific treatment processes; information regarding the presence and concentrations of particular species can assist treatment plant operators in optimizing systems for maximum removal efficiency. Brooks Rand Labs provides cutting-edge analytical methods to quantify metallic species in even difficult matrices, including industrial wastewaters.

Below are just a few of the speciation analyses we offer for arsenic and selenium. For more information, contact a BRL representative today.

arsenate	 selenate
• arsenite	 selenite
 monomethylarsonic acid 	 selenomethionine
 dimethylarsenic acid 	 methylseleninic acid
 arsenobetaine 	 selenocyanate



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Specializing in superior quality trace metals analytical services, Brooks Rand Labs focuses on metals speciation, trace level detection limits, and the analysis of complex matrices.

Experience & Expertise

Since 1982, Brooks Rand Labs has specialized in providing the highest quality trace metals analytical services and instrumentation. Low detection limits, outstanding data quality, and unparalleled customer service have established Brooks Rand Labs as the premier specialty metals analytical laboratory services provider.

As experts in the determination and characterization of trace metals in complex matrices, we have the capabilities to meet even the most challenging project requirements. Ultra-clean, pre-tested sampling equipment delivered directly, fast turn-around-time options, and custom reporting packages at competitive prices ensure that our clients receive the guality data they require to make critical decisions.

Ultra-low Detection and Reporting Limits

Brooks Rand Labs consistently strives to achieve detection and reporting limits that are among the lowest commercially available. Performance based evaluations of laboratory techniques ensure the most accurate and precise measurements at even the lowest concentrations. Ultra-clean

facilities, laboratory equipment, and reagents, custom designed state-ofthe-art instrumentation, and constantly improving methods allow Brooks Rand Labs to provide meaningful metals concentrations data in even the most challenging matrices.

Outstanding Data Quality

As an ultra-low level trace metals analytical laboratory, Brooks Rand Labs appreciates how important high quality data is for our clients. All our data is subjected to a rigorous multi-level review process to ensure only the most credible and scientifically defensible data is provided to our clients

The accuracy and precision of our data are constantly proven by internal and client-requested laboratory audits; consequently, Brooks Rand Labs is proudly NELAP accredited through the State of Florida Dept. of Health and certified in many additional states.

Unparalleled Customer Service

The project management team at Brooks Rand Labs provides clients with an unparalleled level of support from initial project planning, to data validation and interpretation, and project follow-up. They review quality assurance and sampling plans, advise on sampling procedures, and produce custom reporting packages that are superior to other analytical laboratories.