Mercury Capture and Fate Using Wet FGD at Coal-Fired Power Plants

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EXECUTIVE SUMMARY

This paper provides an assessment of the U.S. Department of Energy Office of Fossil Energy's National Energy Technology Laboratory research and development efforts to optimize mercury capture in wet flue gas desulfurization (FGD) systems and characterize the fate of mercury in the resultant by-products. Coal characteristics, combustion conditions, and air pollution control devices upstream of a power plant FGD system have an impact on the types and concentration of flue gas mercury at the FGD inlet. These factors can also affect the amount of mercury removed (co-removal) in the FGD system and the fate of mercury in FGD byproducts. This paper will help to explain the system performance of wet FGD and upstream processes for control of mercury on coal-fired power plants. The first portion of the paper provides background information on regulatory drivers, relative air pollution control technologies (including wet and dry FGD systems, selective catalytic reduction (SCR), activated carbon injection, and oxidation additives), current and projected FGD capacity, co-benefit mercury capture, and FGD by-product utilization and disposal. The second portion addresses the Innovations for Existing Plants program's mercury and coal utilization by-products research areas and provides details on projects related to mercury capture and fate when using wet FGD systems at coal-fired power plants.

Issues of primary concern to the topic of *Mercury Capture and Fate Using Wet FGD at Coal-Fired Power Plants* are: (1) SCR mercury oxidation; (2) mercury oxidation by other methods; (3) mercury capture and re-emission reduction across FGD systems; and (4) the fate of mercury in FGD by-products. NETL-sponsored research is increasing the knowledge and understanding of these issues through field testing and technology development. A summary of key results from this research is provided below:

- Mercury Oxidation Across SCR – The increase in mercury oxidation across SCR systems when firing Eastern bituminous and PRB coals was examined. The amount of oxidation varied, with percentage point increases ranging from 10% to 71%. Variations were possibly due to differences in coal properties, catalyst design, and catalyst age. Oxidation of mercury is significant because FGD systems are more effective at removing oxidized mercury than elemental mercury. Based on the results of this particular set of tests on bituminous and PRB coals, average total mercury removal was 89% and 48% with and without SCR operation, respectively.

- Mercury-Specific Oxidation Catalysts – During testing at a North Dakota lignite-fired unit, the oxidized mercury concentration increased from 34% to 84% across the solid honeycomb Pd #1 catalyst.
- Mercury Re-Emission by Wet FGD – Bench-scale testing and data evaluation suggests that sulfur complexes are major drivers for the chemical reduction of oxidized mercury to elemental mercury that can result in re-emission of mercury from the wet FGD absorber. Preliminary results indicate that low concentrations of chloride can slow the reduction of oxidized mercury to elemental mercury by sulfur, while high concentrations of chloride may completely inhibit the sulfur reactions, preventing the reduction of oxidized mercury to elemental mercury.
- Fate of Mercury in FGD Gypsum During Wallboard Production – Characterization of mercury emissions during wallboard manufacturing using FGD gypsum from five different power plant configurations is currently ongoing. Three configurations showed mercury emissions of 8% or less across the wallboard plant, while one configuration showed 46% emission (although the emissions on a mass basis were not much greater than other configurations). In all configurations, most of the mercury emitted during vent stack testing was found to be elemental mercury (90% or greater). During a separate research project, FGD gypsum feedstock and resulting wallboard products from five wallboard manufacturing plants were analyzed with results indicating three plants with high or nearly complete mercury retention, one plant with a mercury retention of approximately 88% and a fifth plant with a retention rate of only 42%.
- Characterization of Mercury in FGD Gypsum – Researchers also analyzed FGD gypsum and determined that mercury is most likely bound to an iron complex in the FGD gypsum. This finding could provide for possible separation at the power plant of captured mercury from the FGD gypsum. Separation at the power plant would then minimize mercury concentrations in the FGD gypsum feedstock. Additionally, researchers have found that little mercury is emitted during laboratory leaching tests on FGD by-products.

INTRODUCTION

This paper provides an assessment of the U.S. Department of Energy Office of Fossil Energy's National Energy Technology Laboratory (DOE/NETL) research and development (R&D) efforts to optimize mercury capture in wet flue gas desulfurization (FGD) systems and characterize the fate of mercury in the resultant by-products. On May 18, 2005, the U.S. Environmental Protection Agency (EPA) issued a final regulation for the control of mercury emissions from coal-fired power plants, adding to the urgency of these efforts.[1] The Clean Air Mercury Rule (CAMR) establishes a nationwide cap-and-trade program that will be implemented in two phases and applies to both existing and new plants. Based on 1999 power plant emission estimates,[2] the cap-and-trade provision of the rule would reduce mercury emissions by almost 70%, from 48 tons per year (tons/yr) to 38 tons/yr by 2010 and to 15 tons/yr in 2018. EPA has projected that "co-benefit" mercury reductions[a] achieved through further sulfur dioxide (SO_2) and nitrogen

[a] Co-benefit mercury reduction refers to the ability of conventional air pollution control equipment for NOx, PM, or SO_2 to also capture mercury. For example, a wet FGD system is designed primarily for SO_2 removal. However,

oxides (NOx) emission controls required under the Clean Air Interstate Rule (CAIR) will likely enable industry compliance with the Phase I cap. However, both improvements in co-benefit mercury capture and development of new mercury control technologies will be needed to achieve the level of control necessary to meet the Phase II cap. The CAMR preamble speaks to the need for further RD&D in the area of mercury control technology.[1]

To date, use of activated carbon injection (ACI) has shown the most promise as a near-term mercury control technology. DOE/NETL and others are conducting field tests of a number of alternative approaches to enhance ACI mercury capture performance for both bituminous and low-rank coal applications, including the use of chemically-treated powdered activated carbons (PAC) that compensate for low chlorine concentrations in the combustion flue gas. Other mercury control technologies are being tested to enhance mercury capture for plants equipped with wet FGD systems. These FGD-related technologies include: 1) coal and flue gas chemical additives and fixed-bed catalysts to increase levels of oxidized mercury in the combustion flue gas; and 2) wet FGD chemical additives to promote mercury capture and prevent re-emission of previously captured mercury from the FGD absorber vessel. However, once captured in a wet FGD system, it is critical to assure that the mercury is not inadvertently released to the environment. Therefore, DOE/NETL is also conducting R&D on the characterization of potential mercury release in both FGD by-product disposal and utilization applications.

BACKGROUND

The following sections provide brief background information on FGD technology, co-benefit mercury capture, and FGD by-product disposal and utilization.

Flue Gas Desulfurization Technology

FGD Technology Description

Today's commercially-available FGD technologies can achieve 90% to 98% SO_2 capture.[3] The basic process involves spraying a lime or limestone reagent into the FGD vessel. The alkaline reagent reacts with SO_2 and water to form a precipitated salt by-product that can be filtered from the system and either disposed in landfills or recycled for beneficial use. Depending on the type of FGD process, the salt by-product is calcium sulfite (anhydrite) and/or calcium sulfate (gypsum). The FGD process can be further defined as either dry or wet depending on the amount of water used to spray the reagent into the flue gas. Figures 1 and 2 present simple schematics of dry and wet FGD systems, respectively.

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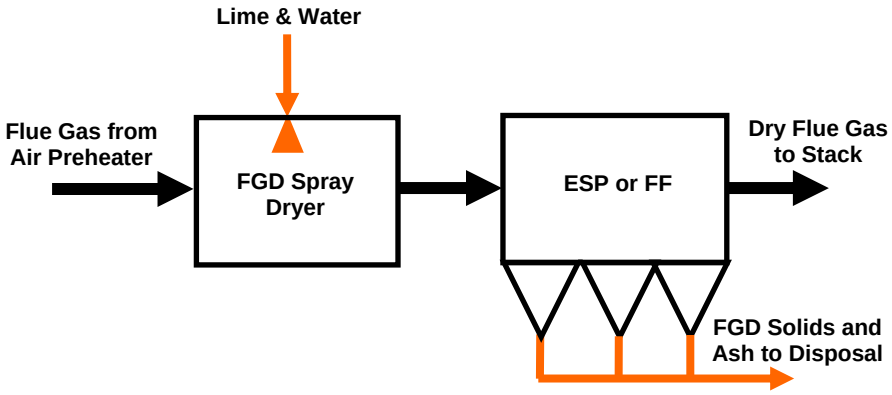
wet FGD can also capture all forms mercury, being most effective at capturing oxidized forms of mercury that are water-soluble.

Figure 1 – Dry FGD Process Schematic



Dry FGD systems can economically achieve 90% to 95% SO_2 capture and are typically used at plants burning low-sulfur coal. However, relatively poor reagent utilization, the main disadvantage of dry FGD systems, increases annual operating costs. Dry FGD systems use a minimal amount of water to cool, but not saturate, the flue gas. Subsequently, the relatively dry calcium sulfite by-product can be captured along with fly ash in a downstream electrostatic precipitator (ESP) or fabric filter (FF). The basic chemical reactions for a dry FGD system with a lime reagent are as follows:

Lime Hydration: $CaO + H_2O \rightarrow Ca(OH)_2$

SO_2 Reaction: $Ca(OH)_2 + SO_2 \rightarrow CaSO_3 \bullet ½H_2O + ½H_2O$

Wet FGD systems can economically achieve 95% to 98% SO_2 capture and are typically used at plants burning high sulfur coal. The main disadvantage of wet FGD systems is the acidic environment that requires construction with corrosion-resistant materials that increase capital costs. In wet FGD systems, there is a large amount of water spray that saturates the flue gas, and the calcium sulfite/sulfate salts must be filtered from the ensuing FGD slurry that is collected at the bottom of the absorber vessel. With most wet FGD systems, an ESP or FF is used upstream to separately remove fly ash from the flue gas. The relative amount of calcium sulfite/sulfate formed in a wet FGD system is a function of several process parameters, including the amount of oxygen available in the flue gas to convert the sulfite to sulfate. The basic chemical reactions for a wet FGD system with a limestone reagent are as follows:

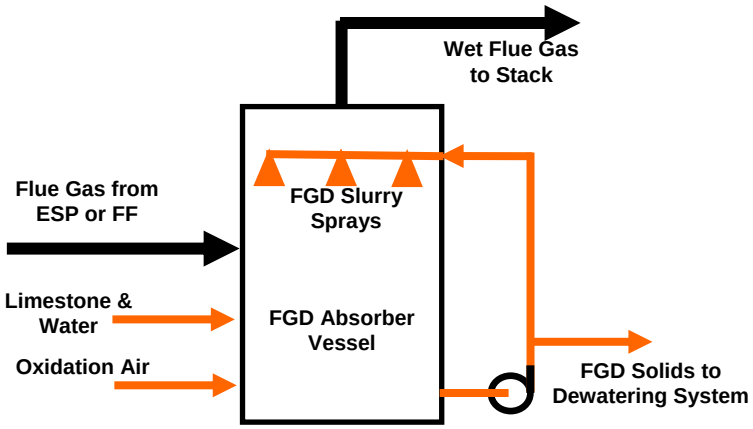
SO_2 Reaction: $CaCO_3 + SO_2 + ½H_2O \rightarrow CaSO_3 \bullet ½H_2O + CO_2$

Sulfite Oxidation: $CaSO_3 \bullet ½H_2O + ½O_2 + 3/2H_2O \rightarrow CaSO_4 \bullet 2H_2O$

A majority of today's wet FGD systems use forced oxidation to further drive the FGD chemistry to maximize calcium sulfate production. Forced oxidation can be completed within the absorber vessel – *in-situ* oxidation – or within a separate holding tank – *ex situ* oxidation. The use of forced oxidation to promote calcium sulfate formation has two primary FGD process benefits: 1) there is less scaling of internal FGD components, which increases performance and reliability;

and 2) dewatering and disposal of calcium sulfate is easier and less expensive than calcium sulfite.

Figure 2 – Wet FGD Process Schematic



Gypsum formed in FGD units can be used in the production of wallboard as a low-cost alternative to naturally-occurring rock gypsum. As a result, many coal-fired power plants equipped with forced oxidation wet FGD systems have been selling their FGD synthetic gypsum by-product to wallboard manufacturers, eliminating the cost of disposal and providing some additional revenue. In addition to other physical and chemical parameters, wallboard manufacturers have quality control specifications for the particle size distribution of FGD synthetic gypsum. As a result, some power plant FGD systems utilize a hydroclone in the FGD solids dewatering system to remove unwanted "fines" from the gypsum – known as fines blow down – prior to shipment to the wallboard manufacturer.

The installation of an FGD system for SO_2 control represents a significant capital investment for coal-fired power plants. The retrofit of a dry lime FGD system for a plant burning low-sulfur bituminous coal is estimated at $155/kW. For a plant burning high-sulfur bituminous coal, the retrofit of a wet limestone FGD system is estimated at $172/kW.

U.S. Current and Future FGD Capacity

The Clean Air Act Amendments of 1990[4] addressed numerous air quality problems in the United States that were not entirely covered in earlier legislation. One of these problems was acid rain deposition caused by SO_2 and NOx emissions from fossil-fueled electric power plants and, to a lesser extent, from other industrial and transportation sources. The legislation set a goal of reducing annual SO_2 and NOx emissions by 10 million tons and 2 million tons below 1980 levels, respectively. As a result, many coal-fired power plants installed low-NOx burners for NOx control and FGD systems for SO_2 compliance. Table 1 provides a summary of the power generation capacity equipped with FGD controls as of 2004, categorized by coal rank and FGD type.[5]

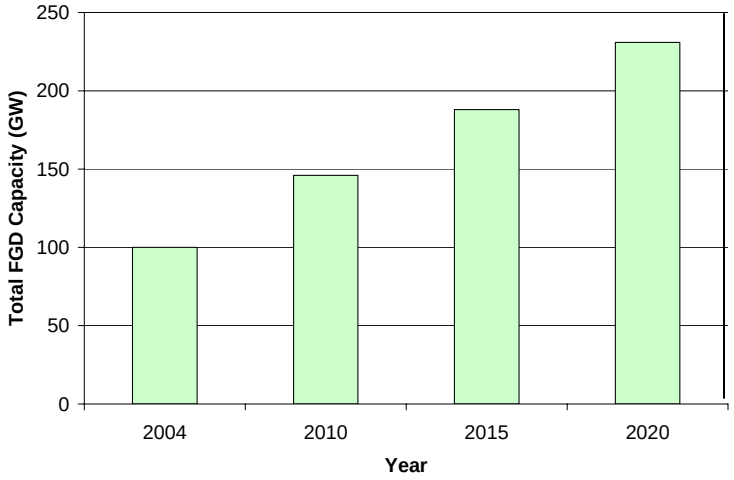
Table 1 – 2004 U.S. Coal-Fired Generation Capacity with FGD Controls, GW

	Bituminous	Subbituminous	Lignite	Total
Wet FGD	57	24	9	90
Dry FGD	4	5	1	10
Total FGD	61	29	10	100
Total Coal-Fired	213	96	15	324

The use of FGD at coal-fired power plants will increase significantly over the next 15 years due to the implementation of CAIR that establishes a market-based allowance cap-and-trade program to permanently cap emissions of SO_2 and NOx in 28 eastern U.S states and the District of Columbia. The SO_2 emission caps were based on percent reductions from the total number of Title IV, Phase II allowances currently allocated to sources in the affected states - a 50% reduction for 2010 and 65% reduction for 2015. When fully implemented, CAIR will reduce SO_2 emissions by more than 70 percent from 2003 levels.

Currently about 100 GW of coal-fired power plant capacity in the United States is equipped with FGD technology. It is anticipated that in response to the SO_2 regulations under CAIR and the co-benefit removal of mercury driven by the CAMR, many coal-fired power plants will install FGD systems. Figure 3 provides a summary of EPA's projection of future FGD capacity in 2010, 2015, and 2020 based on the power generation industry's compliance with CAIR.[6] Total FGD capacity is projected to increase to 231 GW by 2020. Although not identified in the referenced EPA report, based on previous Integrated Planning Model (IPM) runs conducted for the proposed CAIR rule, EPA projected that dry FGD capacity would increase from 10 GW to 21 GW by 2015 with the balance of new FGD retrofits being wet systems.

Figure 3 – Projected Increase in U.S. Coal-Fired FGD Capacity



Co-benefit Mercury Capture

Previous testing funded by DOE/NETL and EPA demonstrated that some degree of co-benefit (i.e., baseline) mercury control is achieved by existing conventional air pollution control devices (APCD) installed for removing NOx, SO_2, and particulate matter (PM) from coal-fired power plant combustion flue gas. Mercury is present in flue gas in varying percentages of three general forms: particulate-bound mercury, oxidized mercury (primarily mercuric chloride – $HgCl_2$), and elemental mercury. The term speciation is used to describe the relative proportion of the three forms of mercury in the flue gas. Mercury speciation affects co-benefit mercury control achieved by existing APCD. For example, elemental mercury is not readily captured by existing APCD, while particulate-bound mercury is captured by ESP and FF. Oxidized mercury is water-soluble and therefore readily captured in FGD systems. Consequently, the mercury capture efficiency of FGD systems depends largely on the fraction of oxidized mercury at the FGD inlet.[7] The following a few factors that affect the oxidized mercury concentration in combustion flue gas, which influences the level of co-benefit mercury capture across FGD systems.

- *Coal chlorine content* – Previous testing revealed that coals with greater than 500 parts per million by weight (ppmw) of chlorine have less than approximately 20% elemental mercury entering the APCD configuration.[7]

- *Unburned carbon in fly ash* – Testing showed that unburned carbon can adsorb vapor-phase mercury to form particulate-bound mercury. In the presence of sufficient chlorine compounds, unburned carbon can also serve as a mercury oxidation catalyst.

- *Temperature upstream of the APCD* – Oxidation of elemental mercury occurs in the temperature range from 850 °F to 300 °F. As a result, the temperature gradient across an air heater (AH) can impact mercury oxidation.

Operation of selective catalytic reduction (SCR) for NOx control is also effective in converting elemental mercury to oxidized mercury that can be subsequently captured in a downstream FGD absorber.[8] SCR units have the potential to achieve high levels of NOx control by reducing NOx to nitrogen gas (N_2) and water vapor (H_2O) in the presence of ammonia and a fixed catalyst.[b] The potential mercury oxidation that occurs across SCR catalysts represents one control method currently under investigation by DOE/NETL and others to enhance removal of elemental mercury. However, the degree of SCR mercury oxidation is variable and appears to be coal-specific due to variations in coal chlorine content and the level of unburned carbon in the fly ash.[c] For example, a series of tests to understand mercury oxidation across SCR systems firing Eastern bituminous and PRB coals found the average percentage point of oxidation to increase by 10% to 71% across the SCR. The average mercury removal without SCR operation was 48% while average mercury removal with SCR operation was 89%.

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[b] Recent experience with SCR indicates that NO_x emission rates as low as 0.05 lb/MMBtu are achievable. According to EPA, approximately 154 GW of SCR will have been installed on U.S. coal-fired power plants by 2020 for compliance with the NOx SIP (state implementation plan) Call Rule and CAIR.

[c] Other factors that influence mercury oxidation across an SCR catalyst include the SCR catalyst space velocity and formulation, the SCR catalyst temperature and age, and coal sulfur content.

Testing funded by DOE/NETL revealed that bituminous coal-fired units exhibit higher concentrations of oxidized mercury at the SCR outlet than similarly equipped units burning subbituminous and lignite coals.[9] Mercury measurement campaigns sponsored by DOE/NETL and the Electric Power Research Institute (EPRI) showed that more than 70% of the mercury at the SCR outlet can be oxidized if the coal chlorine content is greater than about 500 ppmw. In addition, analysis of Ontario Hydro (OH) measurements conducted at bituminous coal-fired units during DOE/NETL's mercury field testing program revealed that: (1) the average elemental mercury concentration is arithmetically reduced by approximately 32% across an SCR NOx reduction system; and (2) the average elemental mercury concentration is arithmetically reduced by approximately 53% across an SCR and APH combination.

Co-benefit mercury capture across existing APCD can vary significantly based on mercury speciation, coal properties, fly ash properties (including unburned carbon), specific APCD configurations, and other factors, with the level of control ranging from 0% to more than 90%. Table 2 presents a summary of average co-benefit mercury capture for various APCD configurations and coal ranks based on OH measurements conducted by: (1) EPA in 1999 as part of their mercury Information Collection Request (ICR) campaign; and (2) DOE/NETL during mercury control technology field testing since 1999. In general, plants burning subbituminous and lignite coals demonstrated lower co-benefit mercury capture than similarly equipped bituminous-fired plants. The lower performance observed for these low-rank coals was linked to higher levels of elemental mercury, associated with the coal's low chlorine content. These data also demonstrate the improved mercury capture effectiveness of wet FGD systems when an upstream SCR NOx reduction system is in-service. For example, average mercury capture for bituminous coal-fired plants equipped with a cold-side ESP and wet FGD increased from 69% to 86% with the addition of an SCR. FGD systems are more efficient at mercury removal with upstream SCR systems; however FGD systems also remove significant mercury quantities without an SCR system. For example, average mercury capture for bituminous coal-fired plants equipped with a cold-side ESP increases from 28% to 69% with the addition of wet FGD. Average mercury capture for plants with a FF increases from an average of 90% to 98% with the addition of wet FGD.

Table 2 also displays the range of mercury removal values for each coal-rank / APCD subset. As mentioned above, co-benefit mercury capture across existing APCD can vary significantly based on coal and fly ash properties; however, the variability shown in Table 2 may also be a function of OH measurement error. For example, baseline mercury capture ranges from 0% to 92% for a bituminous-fired unit equipped with a CS-ESP. For this analysis, the range in baseline mercury capture was developed by setting any negative mercury removal values (indicating mercury formation) equal to zero.

Table 2 – Average Co-benefit Mercury Capture by Coal Rank and APCD Configuration

APCD Configuration	Overall Average Percentage Mercury Capture				
	Bituminous		Subbituminous		Lignite
	w/o SCR	w/ SCR	w/o SCR	w/ SCR	w/o SCR
CS-ESP	28 (0 - 92)	8 (0 – 18)	13 (0 – 61)	69 (58 – 79)	8 (0 – 18)
CS-ESP + Wet FGD	69 (41 – 91)	85 (70 – 97)	29 (2 – 60)	NA	44 (21 – 56)
HS-ESP	15 (0 – 43)	NA	7 (0 – 27)	NA	NA
HS-ESP + Wet FGD	49 (38 – 59)	NA	29 (0 – 49)	NA	NA
FF	90 (84 – 93)	NA	72 (53 – 87)	NA	NA
FF + Wet FGD	98 (97 – 99)	NA	NA	NA	NA
SDA + FF	98 (97 – 99)	95 (89 – 99)	19 (0 – 47)	NA	4 (0 – 8)
SDA + CS-ESP	NA	NA	38 (0 – 63)	NA	NA
PS	NA	NA	9 (5 – 14)	NA	NA
PS + Wet FGD	32 (7 – 58)	91 (88 – 93)	10 (0 – 74)	NA	33 (9 – 51)

CS-ESP = cold-side ESP; HS-ESP = hot-side ESP; PS = particulate scrubber; SDA = spray dryer adsorber

FGD By-Product Disposal and Utilization

Over 900 million tons of coal is used annually in the United States, 90% of which is burned for electricity generation, mostly at pulverized coal-fired power plants.[10] The combustion of coal and cleaning of flue gases produces a large volume of material or residue, collectively referred to as coal utilization by-products (CUB). CUB include fly ash, bottom ash, boiler slag, fluidized bed combustion (FBC) ash, and FGD material. Currently, CUB from coal-fired power plants are regulated by EPA under the Resource Conservation and Recovery Act (RCRA). RCRA solid wastes are categorized as either hazardous or non-hazardous. Hazardous wastes are federally regulated under RCRA Subtitle C, while non-hazardous wastes are state regulated under RCRA Subtitle D. In its 1999 Report to Congress, EPA determined that CUB did not generally exhibit any of the four characteristics of a hazardous waste: corrosivity, reactivity, ignitability, and toxicity. Consequently, CUB are currently categorized as non-hazardous wastes under RCRA and most state regulations. The continued regulatory categorization of CUB as non-hazardous solid wastes is obviously an important factor in minimizing the cost of disposal and is critical to CUB marketability for beneficial use applications.

The American Coal Ash Association (ACAA) estimated that in 2004, a total of 122 million tons of CUB were produced in the United States.[11] Approximately 73 million tons (60%) of CUB were disposed in either landfills or impoundments, while the remaining 49 million tons (40%) were recycled for use in a variety of beneficial applications. Some of the major beneficial

applications for CUB include use as a partial substitute for Portland cement in concrete (fly ash), structural fill material (bottom and fly ash), blasting grit (boiler slag), and wallboard manufacture (FGD gypsum).[12] In particular, the utilization of FGD gypsum as a feedstock for wallboard production was spurred by widespread deployment of FGD systems to curtail SO_2 emissions.

A summary of 2004 ACAA estimates for FGD by-product production and use is provided in Table 3. Of the total 31 million tons of FGD by-product generated in 2004, approximately 10 million tons (33%) were recycled for various beneficial applications. In 2004, eighteen U.S. coal-fired power plants sold approximately 8 million tons of FGD gypsum to the wallboard industry, representing the largest beneficial application of FGD by-products.[13] The utilization, rather than disposal, of FGD gypsum can provide significant economic benefits to coal-fired power plant operators. Based on ACAA estimates, the cost for CUB disposal ranges from $3 to $30 per ton, while revenue for CUB utilization typically ranges from $3 to $35 per ton. As a result, the combined potential economic benefit for CUB utilization could range from $6 to $65 per ton. The wide range of costs and revenues is a result of location, disposal method, transportation, and market supply and demand. Utilization of FGD gypsum also provides significant secondary benefits such as reduced land requirements for disposal, conservation of natural resources, and lower production costs for wallboard manufacturers.

Table 3 – ACAA Survey of FGD By-Product Production and Use in 2004, Tons

	FGD Gypsum	FGD Material Wet Scrubbers	FGD Material Dry Scrubbers	FGD Other	Total FGD
FGD Byproduct Disposal	2,905,045	16,304,123	1,652,350	112,305	20,973,823
FGD Byproduct Utilization	9,044,955	1,195,877	177,480	3,291	10,421,603
Total FGD Byproduct	11,950,000	17,500,000	1,829,830	115,596	31,395,426
% Utilization	75.7%	6.8%	9.7%	2.8%	33.2%
Utilization Applications					
Concrete/Concrete Products/Grout	291,439		37,343		
Cement/ Raw Feed for Clinker	449,063	39,378			
Flowable Fill			11,274		
Structural Fill/Embankments		266,651			
Mining Applications		282,033	122,589		
Wallboard	8,148,078				
Waste Stabilization/Solidification		338			
Agriculture	131,058	10,593	2,775		
Aggregate			3,499		
Miscellaneous/Other	25,317	596,884		3,291	

U.S. Gypsum Supply and Demand

In 2005, total U.S. consumption of gypsum was approximately 41.7 million tons.[14] According to the U.S. Geological Survey (USGS), over 39.6 million tons (88%) of total U.S. gypsum consumption was used in the manufacture of wallboard and other plaster products. The use of

synthetic gypsum (primarily FGD gypsum by-product) contributed 10.2 million tons (24%) of total consumption in 2005. For comparison, the reuse of FGD gypsum in 1994 accounted for only six percent of all gypsum used in North America.[15] Therefore, the current level of FGD gypsum utilization indicates a significant growth in the market for FGD gypsum as a feedstock for wallboard production in just over ten years.

The low cost and ready availability of FGD gypsum compared to rock gypsum will continue to encourage wallboard manufacturers to select FGD gypsum and site their new wallboard plants close to coal-fired utilities that produce marketable gypsum. The construction of wallboard manufacturing plants near both power plants and population centers[d] increases the sustainable design of the wallboard product by reducing transportation and use of fossil fuels. Most gypsum wallboard plants constructed since 1998 use synthetic gypsum to fulfill all or part of their raw material requirements. For example, BPB, a manufacturer and marketer of wall and ceiling products throughout North America, recently announced the completion of long-term agreements with American Electric Power (AEP) and Progress Energy for a secure, long-term source of high-quality synthetic gypsum.[16] The synthetic gypsum will serve as a feedstock for BPB's new wallboard plants to be built in Marshall County, West Virginia and Roxboro, North Carolina.

The projected increase in wet FGD capacity will cause a substantial increase in the volume of FGD gypsum being produced. Table 5 presents projections of FGD by-product production and gypsum demand. DOE/NETL estimates that FGD by-product production could increase from 31 million tons in 2004 to approximately 86 million tons in 2020 based on the EPA projection for additional FGD capacity, and the U.S. Department of Energy, Energy Information Administration's (DOE/EIA) projection of increased electricity demand.

Table 5 – Projected Increase in FGD By-Product Generation, and U.S. Gypsum Demand

	2010	2015	2020
Total Generation of FGD By-products (million tons)	47	62	86
Total U.S. Demand for Gypsum Products (million tons)	44	48	52

Meanwhile, demand for gypsum products in North America is forecast to advance 1.7% annually. Assuming a continuation of 1.7% growth, DOE/NETL estimates that U.S. demand for gypsum products would increase from approximately 40 million tons in 2004 to 52 million tons in 2020. Increasing demand for gypsum depends principally on the strength of the construction industry – particularly in the United States, where about 95% of the gypsum consumed is used for wallboard products, building plasters, and the manufacture of Portland cement. The projected large growth in production of FGD by-products coupled with the relatively low growth in demand for gypsum, could result in a significant increase in the disposal of FGD by-products unless other utilization markets can be developed.

[d] Traditionally, wallboard plants are constructed near large gypsum deposits that are concentrated in the Great Lakes region, mid-continental region, and several Western states. The uneven distribution of natural gypsum leads to high transportation costs for refined wallboard products, and facilitates the importation of crude gypsum from Canada and Mexico.

NETL'S MERCURY AND CUB R&D PROGRAMS

DOE/NETL is carrying out comprehensive mercury research under the DOE Office of Fossil Energy's Innovations for Existing Plants (IEP) Program.[17,18] The IEP Program includes two complimentary research areas – development of mercury emissions control technologies and CUB characterization. Working collaboratively with power plant operators, EPRI, academia, state and local agencies, and EPA, the two research areas have greatly advanced our understanding of the transformation in flue gas, capture, and fate of mercury from coal-fired power plants. This research directly supports the need for advances in technology to comply with CAMR.

Initial efforts in the early 1990s were directed at characterizing power plant mercury emissions and focused on laboratory- and bench-scale control technology development. The mercury emissions control technology R&D program is currently directed at full-scale and slip-stream field testing of mercury control technologies, as well as continued bench- and pilot-scale development of novel control concepts. The near-term goal is to develop mercury control technologies that can achieve 50-70% mercury capture at costs 25-50% less than baseline estimates of $50,000-$70,000/lb of mercury removed. These technologies would be available for commercial demonstration by 2007 for all coal ranks. The longer-term goal is to develop advanced mercury control technologies to achieve 90% or greater capture that would be available for commercial demonstration by 2010.

CUB research is driven by, and in response to, the transfer of mercury and other trace metals from flue gas to the solid and liquid effluent streams as a result of implementing pollution controls on coal-based power systems. At least partly attributable to DOE's past research efforts directed at environmentally acceptable and safe use of these materials, CUB beneficial utilization has increased from 25% in 1990 to 40% in 2004.[19] Continued environmental characterization and related research is needed in order to achieve a national goal of increasing environmentally acceptable use of CUB to 50% by 2010, and nearly 100% by 2020. However, both achieving and maintaining this goal will be challenging in four respects. First, increasing concern over the fate of mercury and other trace metals removed from the power plant flue gas and captured in by-products will bring about increased scrutiny as to how these materials are to be utilized and disposed. Second, the installation of FGD technology to comply with SO_2 regulations could significantly increase the amount of solid material generated by coal-fired power plants. Third, injection of sorbents such as powdered activated carbon (PAC) to control mercury could negatively impact the sale of fly ash and FGD gypsum for cement and wallboard. Finally, NOx controls could also negatively impact beneficial utilization of fly ash due to excessive levels of unburned carbon and/or ammonia.

Mercury Technology R&D

Initiated in 2001, DOE/NETL's Phase I mercury control field testing program included an evaluation of ACI using conventional activated carbon sorbents at four power plants and an evaluation of a proprietary chemical additive at two power plants to improve mercury capture in wet FGD systems.[20] In September 2003, DOE/NETL selected eight new projects to test and

evaluate various mercury control technologies under a Phase II, Round 1 solicitation that included two projects to enhance mercury capture in wet FGD systems using fixed bed catalysts and chemical additives to promote mercury oxidation. Phase II, Round 1 field testing began in 2004 and was completed in the 1st quarter 2006. An additional six projects, representing seven technologies, were subsequently awarded in October 2004 under a Phase II, Round 2 solicitation that began 2nd quarter 2005 and are scheduled for completion in 2007. One of the Phase II, Round 2 projects involves testing a chemical additive for prevention of mercury re-emission from wet FGD systems. In February 2006, DOE/NETL announced the selection of twelve new mercury control projects under a Phase III solicitation that includes full-scale field testing of fixed bed oxidation catalysts to enhance wet FGD mercury capture. Table 6 includes a brief description of these FGD-related mercury control technology field testing R&D projects. Additional NETL mercury program projects addressing mercury oxidation and capture via FGD are listed in Table 7.

Table 6 – DOE/NETL Wet FGD-Related Mercury Control Technology Field Testing R&D Projects

Mercury Control Technology and Researcher				
Host Company	**Plant Site**	**Coal Type**	**APCD Configuration**	**Test Status**
Phase I: Chemical Additive for Enhanced Mercury Control in Wet FGD – B&W				
MSCPA	Endicott	Bituminous	ESP & Wet FGD	Complete 2002
AEP	Zimmer	Bituminous	ESP & Wet FGD	Complete 2002
IP&L	Petersburg Unit 2	Bituminous	LSFO with fines blowdown & wet FGD	Complete 2006
Phase II, Round 1: Catalysts to Promote Mercury Oxidation Upstream of Wet FGD Systems – URS				
Great River Energy	Coal Creek Unit 1	North Dakota Lignite	ESP & Wet FGD	Complete 2004
City Public Service of San Antonio	J.K. Spruce	PRB	FF & Wet FGD	Complete 2005
TXU	Monticello Unit 3	Texas Lignite	ESP (452 SCA) & Wet FGD	Began 1st Q 2005
Southern	Yates Unit 1	Bituminous	ESP (173 SCA) & Wet FGD	Began 4th Q 2005
Phase II, Round 1: Chemical Additives to Promote Mercury Oxidation Upstream of Wet FGD Systems – UNDEERC				
Minnkota Power	Milton R. Young Unit 2	North Dakota Lignite	ESP (375 SCA) & Wet FGD	Complete 2005
TXU	Monticello Unit 3	Texas Lignite	ESP (452 SCA) & Wet FGD	Complete 2005
Phase II, Round 2: Chemical Additive for Prevention of Mercury Re-Emission from Wet FGD – URS				
TXU	Monticello Unit 3	Texas Lignite	ESP (452 SCA)	Complete 2005
Southern	Yates Unit 1	Bituminous	ESP (173 SCA) & Wet FGD	Begin 4th Q 2006
Phase III: Full-Scale Testing of Mercury Oxidation Catalyst Upstream of a Wet FGD System – URS				
LCRA	Fayette Unit 3	PRB	ESP & Wet FGD	Begin 4th Q 2007

Table 7 – DOE/NETL Wet FGD-Related Mercury R&D Projects

Project Title	Research Organization
Evaluation of Mercury Emissions from Coal-Fired Facilities with SCR-FGD Systems	CONSOL Energy Inc.
Preliminary Field Evaluation of Mercury Control Using Combustion Modifications	GE Energy and Environmental Research Corporation
Evaluation of Mercury Speciation at Power Plants Using SCR and SNCR NOx Control Technologies	UNDEERC
Evaluation of the Impact of Selective Catalytic Reduction on Mercury Speciation for a Power Plant Firing a Blended Coal	UNDEERC
Oxidation of Mercury Across SCR Catalysts in Coal-Fired Power Plants Burning Low Rank Flues	Reaction Engineering International
Bench-Scale Kinetics Study of Mercury Reaction in FGD Liquors	URS Group

CUB Technology and In-House R&D

NETL CUB research includes projects sponsored directly by the IEP Program, projects sponsored through the Combustion Byproducts Recycling Consortium (CBRC), and research conducted by NETL In-House researchers. The CBRC partnership integrates the efforts of the electric power industry, State and Federal regulatory agencies, and academia to guide national and regional research priorities, with the mission of promoting and supporting commercially viable and environmentally sound recycling of CUB for productive uses through scientific research, development, and field testing. Table 8 presents wet FGD and mercury-related CUB and In-House R&D projects.

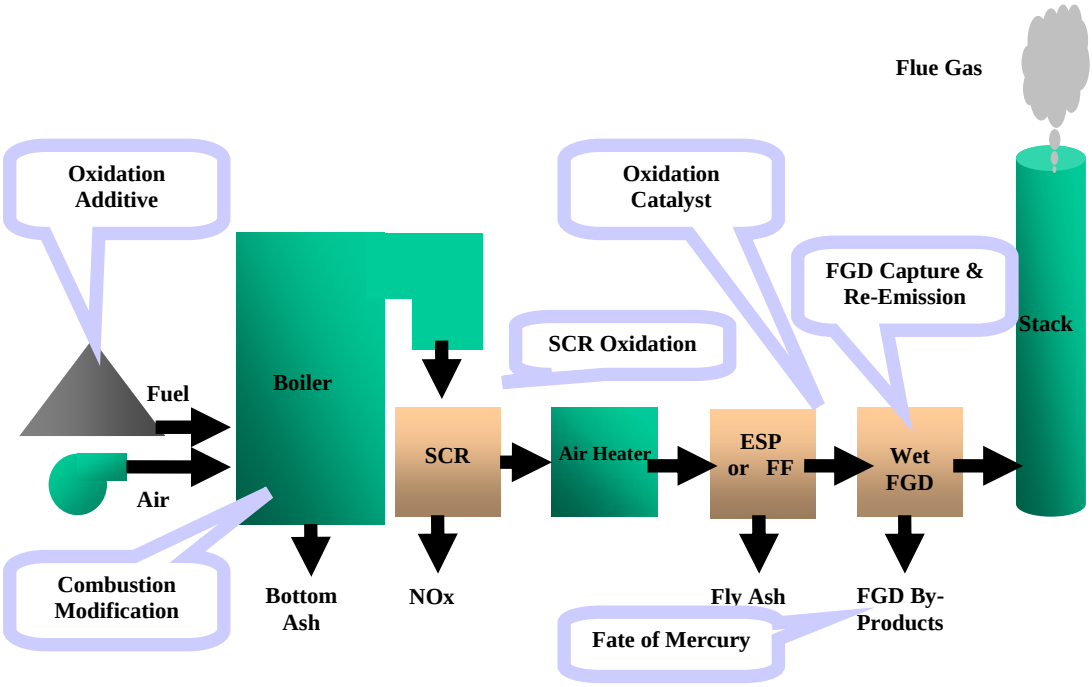
Table 8 – DOE/NETL Wet FGD and Mercury-Related CUB and In-House R&D Projects

Project Title	Research Organization
The Effect of Mercury Controls on Wallboard Manufacture	Tennessee Valley Authority (CBRC)
Fate of Mercury in Synthetic Gypsum Used for Wallboard Production	USG Corporation
Characterization and Management of Mercury from FGD By-Products	NETL In-House

DOE/NETL FGD-Mercury R&D RESULTS

Figure 4 presents a summary of six major areas of DOE/NETL R&D that relate to mercury capture and fate using wet FGD. The focus areas include: combustion modification, SCR oxidation, oxidation catalysts, oxidation additives, FGD capture and re-emission, and fate of mercury in FGD by-products. The following is a detailed discussion of results from individual projects in each of these R&D focus areas.

Figure 4 – DOE/NETL R&D Focus Areas for Mercury Capture and Fate Using Wet FGD



Increasing Oxidized Mercury in Flue Gas

FGD systems are most effective at oxidized mercury removal. The following NETL sponsored projects investigate mercury oxidation enhancement via use of combustion modifications, SCR systems, oxidation catalysts, and/or oxidation additives.

Combustion Modifications

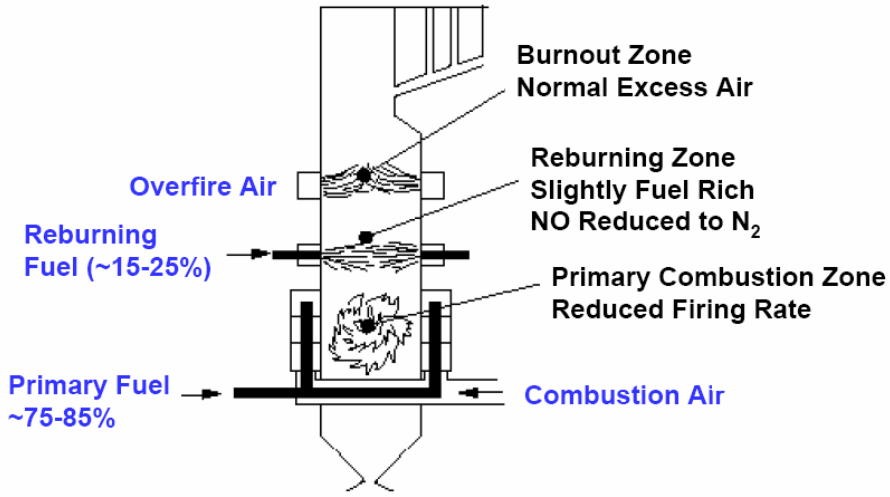
Preliminary Field Evaluation of Mercury Control Using Combustion Modifications

Field evaluation of a novel multi-pollutant control technology was conducted by General Electric Energy and Environmental Research Corporation.[21] Field testing took place at Western Kentucky Energy's Green Station Units 1 and 2 that burn a blend of bituminous coals and are equipped with an ESP and wet FGD. As shown in Figure 5, the technology utilizes coal reburn to achieve reductions in mercury and NOx emissions.

Activities completed have included measurement of mercury emissions in Unit 2 while optimizing the reburn system to minimize loss-on-ignition (LOI) and NOx emissions. Application of coal reburn to Unit 2 is displayed in Figure 5. Similar activities were conducted at Unit 1. Testing indicated that ESP outlet flue gas mercury concentrations ranged from 6 to 10 micrograms per normal cubic meter ($\mu g/Nm^3$) of flue gas. Because the ESP removed particulate bound mercury, the flue gas consisted mainly of oxidized mercury. The high levels of oxidized mercury achievable with the combustion modifications indicate a potential to combine this technology with FGD units to increase mercury removal. Mercury removal across the ESP

ranged from 6% to 40%. Field testing also revealed that mercury capture increased as ESP temperature decreased.

Figure 5 – Application of Coal Reburn to Green Unit 2.[22]



Selective Catalytic Reduction

Evaluation of Mercury Speciation at Power Plants Using SCR NOx Control Technologies

With funding from NETL, the University of North Dakota Energy and Environment Research Center (UNDEERC) evaluated the impacts of SCR on mercury speciation.[23] Mercury measurements were taken at a total of six power plants. As shown in Table 9, testing was initiated at four sites in 2001. Two of these units (Sites S2 and S4) were retested, along with two additional sites, during 2002. Eastern bituminous coals were burned at all locations except for Site S1, which fired Powder River Basin (PRB) subbituminous coal. However, Site S1 was not considered to be representative of a typical PRB-fired unit due to an unusually high level of unburned carbon in the fly ash and the use of a cyclone boiler.

Table 9 – Change in Mercury Oxidation Across the SCR Catalyst.[23]

Site	Year Sampled	Catalyst Type	SCR Inlet Hg^{2+}, % of total Hg	SCR Outlet Hg^{2+}, % of total Hg	Percentage Point Increase,[a] %
S1[b]	2001	Honeycomb	8	18	10
S2	2001	Plate	48	91	43
S2	2002	Plate	54	87	33
S3	2001	Honeycomb	55	65	10
S4	2001	Honeycomb	9	80	71
S4	2002	Honeycomb	33	63	30
S5	2002	Plate	43	76	33
S6	2002	Honeycomb	60	82	22

[a] Defined as (SCR Outlet % - SCR Inlet %).

[b] Site S1 fired a PRB coal; the others were Eastern bituminous coals.

Results of the 2001 and 2002 tests presented in Table 9 show that there was an increase in mercury oxidation across the SCR. However, results indicated that the amount of oxidation across the SCR was highly variable, with percentage point increases ranging from 10% to 71%, and possibly affected by coal properties, catalyst design, and catalyst age.

To discern the overall impact of SCR on mercury speciation, tests were conducted at Sites S2 through S6 both with and without the SCR in-service. This was done by either bypassing the SCR system or testing sister units, one with and one without SCR. Three of the five sites experienced higher concentrations of oxidized and particulate-bound mercury at the SCR outlet during SCR operation. For the other two sites, the percent of oxidized and particulate-bound mercury was greater than 90% both with and without the SCR in operation (note – Table 9 shows percent oxidized mercury and does not include particulate-bound mercury).

UNDEERC also examined the impact of SCR mercury oxidation on mercury removal across downstream wet FGD systems at three coal-fired units. Elemental mercury (Hg^0) concentrations both with and without SCR are presented in Table 10. All sites presented in Table 10 fired bituminous coal. Average mercury removal increased from 48% to 89% with the operation of an SCR. However, the elemental mercury concentration increased across the wet FGD system for both cases (with and without SCR), indicating re-emission of mercury across the vessel. With an upstream SCR in-service, the mercury re-emission phenomenon appeared to be reduced.

Table 10 – Effect of SCR on Hg^0 Concentration Across the Wet FGD.[23]

Site	Year Sampled	FGD Inlet Hg^0 Conc., µg/Nm^3	FGD Outlet Hg^0 Conc., µg/Nm^3	Hg^0 Increase,[a] µg/Nm^3	Total Hg Removal %
With SCR					
S2	2001	0.4[b]	0.9	0.5	89
S2	2002	0.3	1.3	1.0	84
S4	2001	0.5	0.8	0.3	90
S4	2002	1.0	1.3	0.3	91
S5	2002	0.7	1.0	0.3	91
Without SCR					
S2	2001	3.4[2]	5.0	1.6	51
S4	2001	5.6	7.1	1.5	46
S4	2002	5.7	8.0	2.3	44
S5	2002	4.7	6.1	1.4	51

[a] Defined as (FGD Outlet Hg^0 conc. - FGD Inlet Hg^0 conc.).

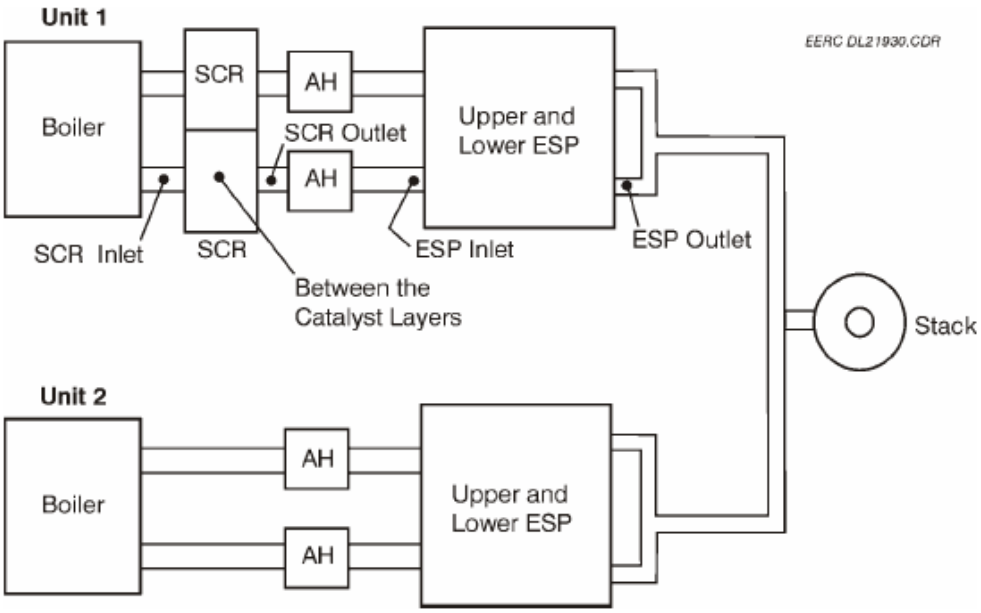
[b] For 2001 Site S2 data, the ESP inlet data were used because the FGD inlet Hg concentration values appear to be clear outliers.

Evaluation of the Impact of Selective Catalytic Reduction on Mercury Speciation for a Power Plant Firing a Blended Coal

Blending of low-sulfur PRB subbituminous coal with Eastern bituminous coal is one method to reduce SO_2 emissions. DTE Energy's Monroe Power Station, which burns a 60% PRB and 40% mid-sulfur Eastern bituminous coal blend, was studied by UNDEERC to determine the impact of

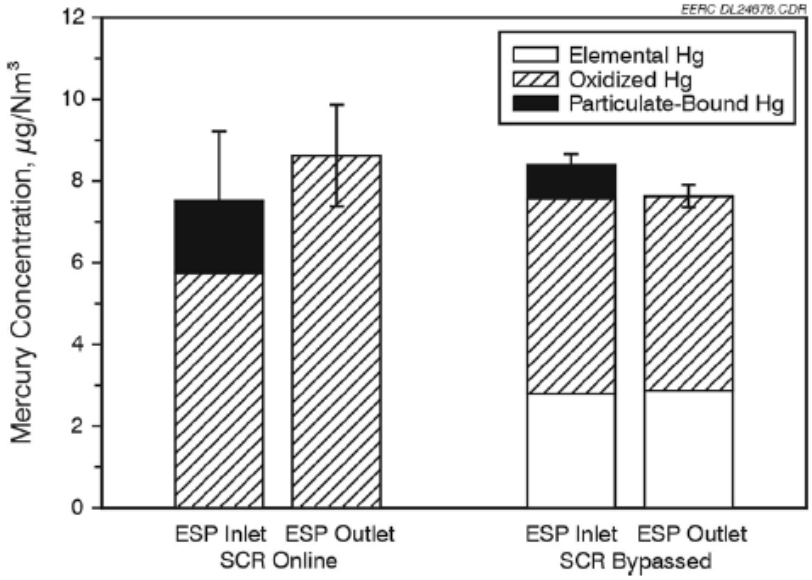
SCR on mercury speciation for blended coal.[24] Tests were conducted at five sampling locations as shown in Figure 6.

Figure 6 – Schematic of Units 1 and 2 Showing Sampling Locations.[24]



As shown in Figure 7, the SCR increased the concentration of oxidized mercury at the ESP inlet.

Figure 7 – The Effect of SCR Operation on Mercury Oxidation at the ESP Inlet and Outlet.[24]



Based on this research, the following conclusions were drawn:[24]

- Substantial oxidation occurred across the SCR. Elemental mercury averaged 40% at the SCR inlet and <1% at the SCR outlet;
- Results did not change substantially between 2003 and 2004, indicating there was little impact of one year of catalyst aging with respect to mercury behavior;
- Limited Mercury removal across the ESP with or without the SCR in-service. The average total mercury emission at the ESP outlet (stack) was 4.9 and 4.7 pounds per trillion British thermal unit (lb/TBtu) with and without the SCR in-service, respectively; and
- As was observed in 2003, the results at Monroe Station were similar to those obtained at plants firing 100% Eastern bituminous coal. The blending of 60% PRB in the coal did not appear to impact the oxidation potential of the SCR, as there was a 41% increase in the concentration of oxidized mercury across the SCR catalyst.

Evaluation of Mercury Emissions from Coal-Fired Facilities with SCR-FGD Systems

Through funding provided by DOE/NETL, CONSOL Energy Inc. conducted mercury speciation measurements at ten coal-fired facilities focused on evaluation of the effect of:[25]

- SCR on mercury capture in the ESP-FGD and SDA-FF combinations at coal-fired power plants;
- Catalyst degradation on mercury capture; and
- Low load operation on mercury capture in an SCR-FGD system

Data collected through this study provided scientific insights into the nature of mercury chemistry in flue gas, the catalytic effect of SCR systems on mercury speciation and the efficacy of different FGD technologies for mercury capture.

Table 11 presents a summary of initial results. In all cases, bituminous coal was used. Plant size ranged from 245MW to 1,300MW and sulfur content ranged from 1.0% to 4.7%. Testing conducted at Sites 8, 9, and 10 included mercury measurements with and without the SCR in operation. In those cases, the percentage of mercury oxidized was higher when the SCR was used. Results from Sites 8, 9, and 10 indicated that the FGD system removed the same percentage of oxidized mercury whether or not the SCR was in operation, but since there was more oxidized mercury when the SCR was operated, there was a corresponding increase in the amount of mercury removed by the FGD system.

The percent elemental mercury oxidation across the SCR/AH combination averaged 96% and 90% with and without the SCR in-service, respectively. Coal-to-stack mercury removal averaged 87% and 72% with and without the SCR in-service, respectively.

Table 11 – Summary of Plant Configuration and Mercury Oxidation and Removal for CONSOL Testing.[25]

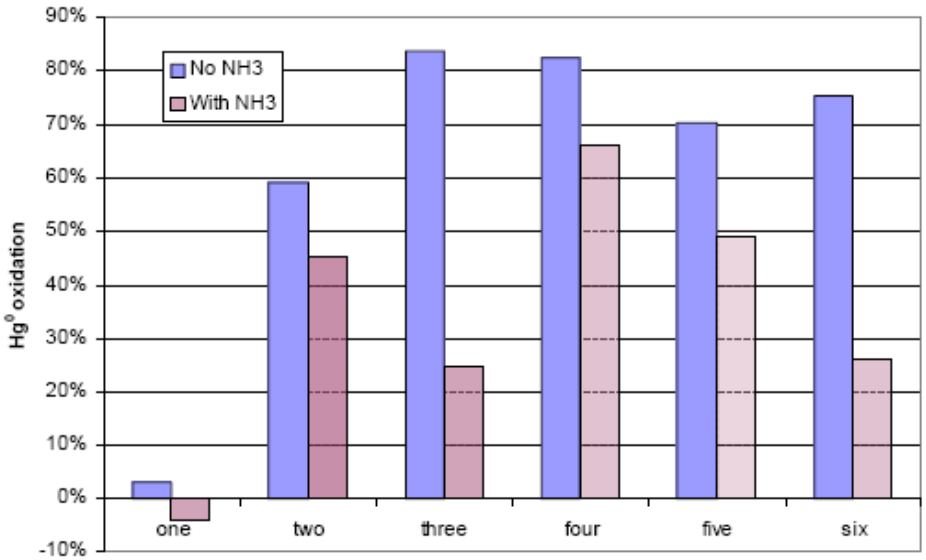
Test Site #	Unit MW	Coal Type	% Sulfur	NOx Control	SO_2 Control	PM Control	% elemental Hg oxidized by SCR and/or AH	Coal-to-Stack, % Hg Removal
1	684	bituminous	4.7	SCR	Lime wet FGD	ESP	90	72[a]
2	330[b]	bituminous	1.0	SCR	Dry FGD w/ SDA	FF	95	87
3	245	bituminous	1.8	SCR	Dry FGD w/ SDA	FF	95	95
4	1,300	bituminous	3	SCR	Limestone wet FGD	ESP	98	86
5	640	bituminous	3.8	SCR	Lime wet FGD	ESP	96	87
6	1,300	bituminous	3.7	SCR	Lime wet FGD	ESP	98	90
7	1,300	bituminous	3	SCR off	Limestone wet FGD	ESP	–	53
8	544	bituminous	3.7	SCR	Limestone wet FGD	ESP	98	83
				SCR off			87	75
9	566	bituminous	3.6	SCR	Limestone wet FGD	ESP	97	86
				SCR off			91	73
10	468	bituminous	1.3 to 1.7	SCR	Limestone wet FGD	ESP	97.4	97
				SCR off			91	87

[a] At this plant, 15% of the flue gas by-passed the FGD because of FGD scrubber capacity limitations.
[b] Actual gross output was between 195 and 221 MW during testing.

Oxidation of Mercury Across SCR Catalysts in Coal-Fired Power Plants Burning Low Rank Fuels

Reaction Engineering International (REI) studied mercury oxidation in a multi-catalyst slipstream reactor to determine optimal catalyst properties at AEP's Rockport Unit 1 that burns a blend of 87% subbituminous and 13% bituminous coal.[26] Five commercial catalysts and one blank monolith were exposed to the flue gas, and gaseous mercury speciation was measured at the inlet and outlet of each catalyst chamber. The five catalysts consisted of three monoliths and two plates. Catalyst pitch ranged from 5.7 to 7.4 mm and chamber porosity ranged from 67.6% to 85.1%. Mercury oxidation across the catalysts ranged from 25% to 65% at typical full-scale space velocities. However, chlorine content of the tested blend was higher than is typical for subbituminous coal. All catalysts showed higher mercury oxidation without ammonia, as shown in Figure 8, indicating ammonia to be a possible hindrance to mercury oxidation. In the figure, one through six represents the different catalysts, with one being the blank.

Figure 8 – Estimated Mercury Oxidation Across SCR Catalyst With and Without Ammonia (NH_3/NO=1.2-2.0).[26]



In addition to the slipstream reactor testing, REI conducted a review of available data on mercury oxidation and developed a global kinetic model of mercury oxidation across an SCR. The data review included examination of the factors that can affect mercury oxidation, which consisted of SCR temperature, space velocity, ammonia presence, sulfur content of coal, and catalyst properties such as the mix between vanadium oxides and other oxides, pore size distribution, and catalyst deactivation over time. The global kinetic model was formulated based on full-scale data and included several factors that can impact mercury oxidation.

Modeling results indicate strategies for maximizing SCR mercury oxidation. Increasing chlorine content of the flue gas (by either blending low-chlorine coal with high-chlorine coal or use of additives) was the recommended method, though lowering flue gas temperature would also increase mercury oxidation.

Oxidation Catalyst

Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems Phase I and II

URS Group is demonstrating at pilot-scale the use of solid honeycomb catalysts, installed downstream of either an ESP or FF, to promote oxidation of elemental mercury in coal combustion flue gas. Because the catalyst is downstream of the particulate control device, catalysts are exposed to an essentially particulate-free flue gas. The subsequent increase in mercury capture across downstream wet lime or limestone FGD systems is being evaluated.[27] Pilot-scale tests will continue for 14 months or longer to provide sufficient full-scale test data to design and implement demonstration-scale installations of the catalytic mercury oxidation technology.

Phase I testing was completed at Great River Energy's (GRE) North Dakota lignite-fired Coal Creek Station (CCS) and City Public Service of San Antonio's J.K. Spruce Plant, which burns a PRB subbituminous coal. These units are equipped with existing wet FGD systems downstream of high-efficiency particulate control devices, an ESP at CCS and a reverse-gas FF at Spruce. The pilot catalyst skids installed at each of these units were loaded with palladium (Pd #1), a commercial NOx SCR catalyst, and an experimental activated carbon (C #6) catalyst. In addition, a subbituminous ash-based (SBA #5) catalyst was installed at CCS, while a gold (Au) catalyst was evaluated at Spruce. Table 12 presents results obtained from CCS when the Pd #1 catalyst was installed upstream of the limestone forced oxidation (LSFO) wet FGD system. The table shows 34% oxidized mercury at the catalyst inlet and 84% oxidized at the outlet. The -39% for elemental mercury removal by the FGD system presented in Table 12 is indicative of re-emission of some of the elemental mercury.

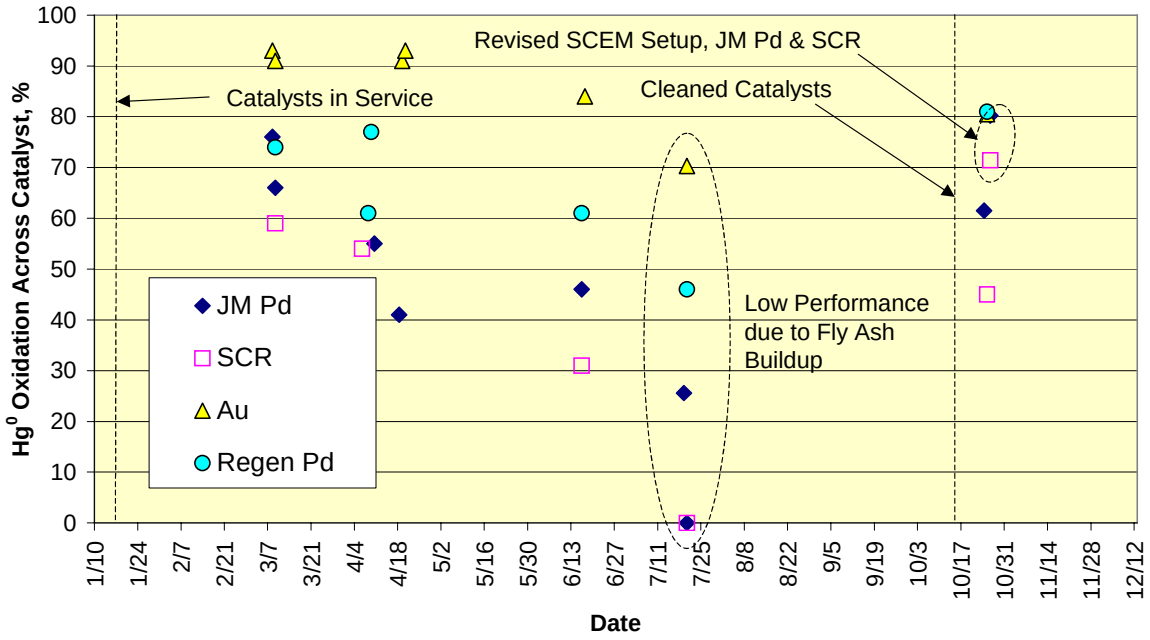
Table 12 – Results of LSFO Pilot Wet FGD Tests at Coal Creek Downstream of Pd #1 catalyst.[28]

	Total Hg	Hg^0	Hg^{2+}	Hg Oxidation, %
Catalyst Inlet (μg/Nm^3)	18.0	11.9	6.1	34
FGD Inlet (μg/Nm^3)	17.4	2.7	14.7	84
FGD Outlet (μg/Nm^3)	3.7	3.8	-0.03	0
FGD Hg Removal (%)	79	-39	100	-

Phase II testing is on-going at TXU's Monticello Steam Electric Station (MoSES) Unit 3 that fires a blend of 80% Texas lignite coal and 20% PRB subbituminous coal. In January 2005, the following mercury oxidation catalysts were installed downstream of the existing ESP at MoSES Unit 3: (1) Au; (2) SCR; (3) regenerated Pd #1 from CCS; and (4) fresh Pd #1. As shown in Figure 9, elemental mercury oxidation after nine months of operation was 81% across the regenerated Pd #1 catalyst, 80% across the Au catalyst, 61% across the fresh Pd #1 catalyst, and 45% across the SCR catalyst. Final results are not yet available.

Additional Phase II testing of the catalytic mercury oxidation technology is being performed at Southern Company's Plant Yates Unit 1 that fires a low-sulfur Eastern bituminous coal. The pilot catalyst skid installed downstream of the existing ESP at this unit was loaded with fresh Pd #1 and Au catalysts, along with regenerated SCR and Au catalysts from J.K. Spruce Plant. Results from Plant Yates Unit 1 are not yet available.

Figure 9 – Catalyst Activity at MoSES Unit 3 after Nine Months of Operation



Oxidation Additive

Large-Scale Mercury Control Technology Testing for Lignite-Fired Utilities – Oxidation Systems for Wet FGD

Evaluation of oxidation additives for mercury control at lignite coal-fired units equipped with ESP and wet FGD pollution controls is the focus of this project.[29] The project team includes UNDEERC, Babcock & Wilcox, EPRI, URS, and ADA-ES. Testing is being conducted at Minnkota Power Cooperative's Milton R. Young (MRY) Unit 2 and TXU's MoSES Unit 3. Research involves establishing mercury oxidation levels upstream of the existing APCD configuration, measuring mercury removal rates across the ESP and FGD, and evaluating the performance of different oxidation additives, also known as sorbent enhancement additives (SEA). Additionally, costs associated with different mercury removal rates will be determined.

Figure 10 is a schematic of MRY Unit 2 showing flue gas sampling locations. Parametric testing at MRY was completed and included evaluation of three mercury oxidation enhancement fuel additives: UNDEERC's SEA1 (an aqueous calcium chloride solution) and proprietary SEA2, and magnesium chloride ($MgCl_2$). Figure 11 is an example of pilot-scale results using a chlorine-containing oxidation additive to lignite coal. SEA2 was found to be the most effective of the additives tested with preliminary data showing 44% mercury removal (without PAC injection) across the ESP/FGD compared to 16% removal by SEA1. With PAC injection, SEA2 yielded removals of 50% or better. SEA2 was selected for longer-term field testing, and preliminary results indicate at least 50% mercury removal rates during 75% of the test when using a small amount of PAC. The possibility of corrosion effects is also being evaluated at this site.

Figure 10 – Schematic of MRY Unit 2 with Sampling Locations.[29]

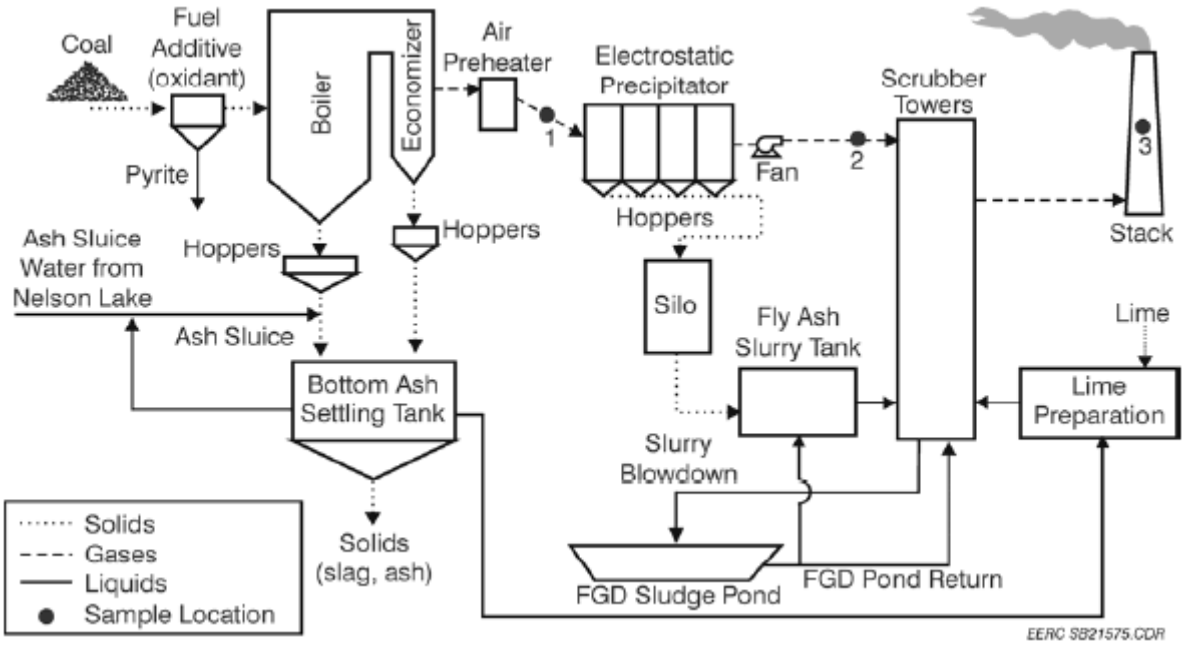
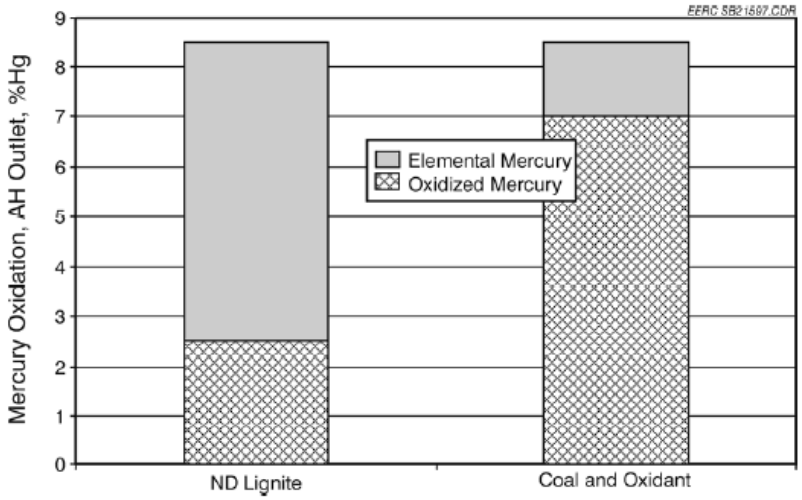


Figure 11 – Oxidation of Mercury by Addition of a Chlorine-Containing Additive to Lignite Coal.[29]



Parametric testing at MoSES Unit 3 using URS's proprietary oxidation additives OA1 and OA2 is in the final stages. Based on preliminary parametric results, URS OA2 was selected for long-term testing. Results from long-term tests are not yet available.

Increasing Oxidized Mercury Capture and Reducing Mercury Re-Emission by FGD

Capture of mercury by FGD systems is one method of meeting CAMR regulations, and research is being conducted to optimize FGD mercury capture. However, field testing has revealed that oxidized mercury captured by the FGD system can be chemically reduced and re-emitted as elemental mercury. As a result, technologies designed to reduce or prevent re-emission of mercury will improve overall efficiency of FGD mercury capture. The following NETL sponsored research projects are examining methods to increase mercury removal across FGD systems by reducing re-emissions.

FGD Kinetics

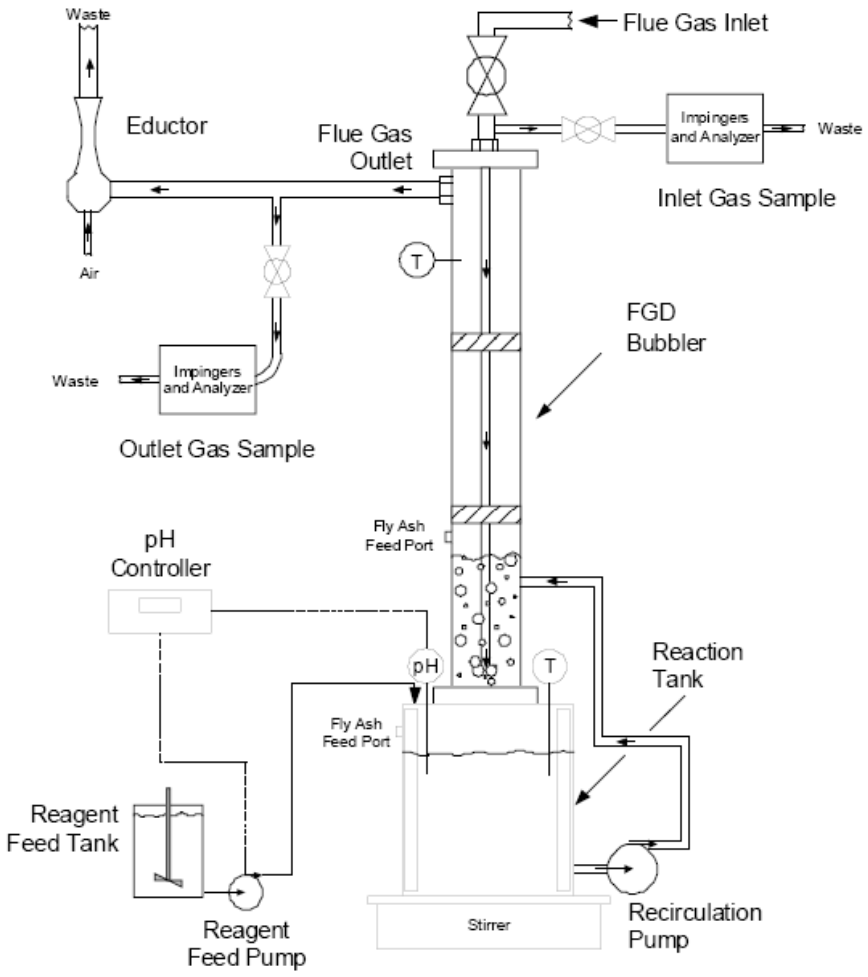
Bench-Scale Kinetics Study of Mercury Reaction in FGD Liquors

URS Group is conducting bench-scale testing to evaluate the reaction kinetics of species in FGD liquors and any resulting chemical reduction and re-emission of mercury.[30] Project goals include: development of a fundamental understanding of the aqueous chemistry of mercury absorbed by wet FGD scrubbing liquors; determination of the chemical reactions that oxidized mercury undergoes once absorbed, the by-products of those reactions, and reaction kinetics; and removal of technology barriers so that mercury capture by wet FGD systems can be maximized.

Ultraviolet/visible light spectroscopy, atomic absorption, and other measurement methods are being used to determine the relative concentration of mercury species, reactants, and by-products over time. Test data are being used to develop a kinetic model to predict mercury reactions in wet FGD systems. The model will be verified by bench-scale wet FGD system tests. The model will be run over a wide range of wet FGD design and operating conditions to determine parameters that minimize mercury re-emissions, maximize mercury capture, and result in captured mercury leaving the system in the by-product solids instead of the blow down liquor. Figure 12 illustrates the bench-scale FGD apparatus used for this project.

Efforts to date have focused on the effects of chloride concentrations, pH, ionic strength, thiosulfate ion concentrations, and iodide concentrations on Mercury re-emission reaction mechanisms and kinetics. Sulfur complexes were found to be major drivers for chemical reduction of oxidized mercury to elemental mercury that can result in re-emission of mercury from the wet FGD absorber. Preliminary results indicate that low concentrations of chloride can slow the reduction of oxidized mercury to elemental mercury by sulfur, while high concentrations of chloride may completely inhibit the sulfur reactions, preventing the reduction of oxidized mercury to elemental mercury.

Figure 12 – URS Bench-Scale FGD Apparatus.[31]



Capture and Re-emission

Full-Scale Testing of Enhanced Mercury Control Technologies for Wet FGD Systems

The goal of this project was to field test mercury control methods for coal-fired units equipped with wet FGD.[32] Babcock & Wilcox and McDermott Technology, Inc. tested a proprietary liquid reagent additive to enhance FGD mercury removal, during field testing at two Ohio bituminous coal-fired utilities in 2001: Michigan South Central Power Agency's (MSCPA's) 55 MW Endicott Station using a limestone wet scrubber with forced oxidation and Cinergy's 1,300 MW Zimmer Station using a Thiosorbic® lime wet scrubber with *ex situ* oxidation.

Field testing at the Endicott Station included the following:

- Parametric testing to define the optimal operating paramenters for the process;

- Two weeks of verification testing to validate the performance of the process with the selected operating conditions; and
- Four months of long-term operation to verify mercury removal rates and demonstrate that there were no detrimental effects on SO_2 removal, materials of construction, or by-product utilization.

Subsequently, testing at Zimmer Station was conducted and consisted of two weeks of verification testing to confirm the performance of the process with the selected operating conditions.

Average mercury removal across the wet FGD system at Endicott Station ranged from 76% to 79%, with most of the oxidized mercury being removed by the wet FGD system. No increase in elemental mercury was observed during testing at Endicott, leading to the preliminary conclusion that the reagent suppressed mercury re-emissions. At Zimmer Station, average mercury removal across the wet FGD system was approximately 51%; however, elemental mercury concentrations continued to increase across the wet FGD system. A summary of baseline and additive test results are presented in Table 13.

Table 13 – Wet FGD Mercury Removal.

	Endicott Verification Test Results		Zimmer Verification Test Results	
Mercury Species	Baseline	Reagent	Baseline	Reagent
Total	~ 60%	76%	~ 45%	51%
Oxidized	~ 90%	93%	~ 90%	87%
Elemental	~ (40%)	20%	~ (20%)	(41%)

Researchers also analyzed mercury concentrations in the major process streams (results are presented in Table 14) and found that mercury in the wet FGD slurry is associated with the fines, rather than the larger gypsum particles or the aqueous phase. This finding is significant because the fines can be separated from the larger gypsum crystals to produce a gypsum product low in mercury content. The fines could then be separately disposed.

Table 14 – Average Mercury Concentration for Major Process Streams.[32]

Hg, ppm (dry)	Endicott	Zimmer
Coal	0.21	0.15
ESP Ash	0.32	0.016
Gypsum	0.70	0.055
Wet FGD Slurry	0.76	0.49
Wet FGD Slurry Fines	38 (by TDT)[a]	13.3

[a] TDT, Thermal Dissociation Test. The fines are not separated at Endicott, so fines were separated in the lab to obtain the values shown above.

Field Testing of a Wet FGD Additive for Enhanced Mercury Control

The objective of this URS project is to field test a wet FGD additive, Degussa Corporation's TMT-15, to prevent the re-emission of elemental mercury in flue gas exiting wet FGD systems.[33]

TMT-15 is used extensively to prevent mercury re-emissions from wet FGD systems on municipal waste incinerators in Europe; however, this project is the first known field test of the additive at a U.S. power plant. Pilot- and full-scale tests of the wet FGD TMT-15 additive are being conducted to determine additive dosage requirements to prevent elemental mercury re-emissions, and to separate mercury from the normal FGD by-products for the following coal types: low-sulfur Eastern bituminous coal, high-sulfur Eastern bituminous coal, and a Texas lignite/PRB coal blend.

The project team consists of URS Group Inc., EPRI, TXU Generating Company LP, Southern Company, and Degussa Corporation. Testing includes: pilot-scale additive testing for Texas lignite; full-scale additive testing for high-sulfur Eastern bituminous coal; pilot-scale additive testing for low-sulfur Eastern bituminous coal (Plant Yates); and full-scale additive tests at Plant Yates.

Figure 13 – Effects of TMT Addition on FGD Liquor Total Mercury Concentration, µg/L.[33]

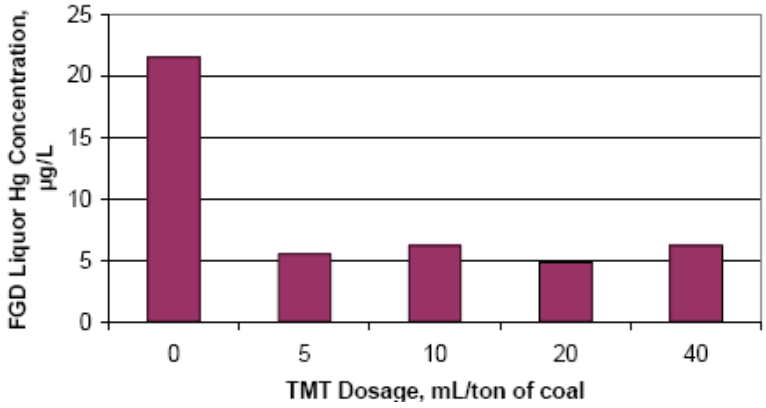


Figure 13 shows the effects of TMT-15 addition on mercury concentrations in the FGD liquor. TMT-15 dosage of 5 milliliters per ton (mL per ton) of coal reduced mercury concentration from greater than 20 micrograms per liter (µg/L) to approximately 5 µg/L. At dosage rates greater than 5 mL/ton, the performance of the TMT-15 additive was similar. Pilot-scale results presented in Table 15 show that after fines separation, gypsum mercury concentration was 1.7 micrograms per gram (µg/g) without the additive and ranged from 1.0 to 1.2 µg/g with the additive.

During pilot-scale parametric testing at TXU's MoSES Unit 3, no evidence was seen of re-emission of mercury, even without using the additive, thus little conclusive information on the ability of TMT-15 to prevent mercury re-emissions was collected at pilot-scale. Results showed TMT-15 to be capable of lowering gypsum by-product mercury concentrations if some form of fines separation is employed to remove mercury laden fines. Full-scale testing is in progress, but test results are not yet available.

Table 15 – Effects of TMT Addition on FGD Gypsum Mercury Concentrations.[33]

TMT Dosage (mL/ton of coal)	Wt% Gypsum Phase in Slurry	Gypsum Hg Content, µg/g (% of Hg in slurry)	Wt% Fines in Slurry	Fines Hg Content, µg/g (% of Hg in slurry)
0	11.6	1.7 (53%)	0.3	55 (44%)
5	9.2	1.2 (33%)	0.5	39 (65%)
10	10.7	1.2 (36%)	0.3	75 (62%)
20	10.0	1.0 (33%)	0.4	52 (63%)
40	9.3	1.2 (36%)	0.3	57 (61%)

Fate of Mercury in FGD By-Products

Continued regulatory categorization of CUB as non-hazardous solid wastes is an important factor in minimizing the cost of CUB disposal and is critical to CUB marketability for beneficial use applications. In particular, the fate of mercury is a concern with regard to future waste characterization. The following NETL sponsored research programs are examining the fate of mercury in FGD by-products.

The Effect of Mercury Controls on Wallboard Manufacture

The goals of this work conducted by Tennessee Valley Authority (TVA) were to: (1) produce in the laboratory high mercury concentrations in FGD material; (2) determine mercury volatilization effects on wallboard manufacture and mercury leaching; and (3) analyze volatilization and leaching procedures for use in indirectly determining mercury forms in FGD gypsum.[34] TVA researchers evaluated three sources of FGD gypsum for mercury release mechanisms: mercury-amended commercial calcium sulfate, FGD material from a laboratory-scale wet FGD system, and FGD material from an operating FGD system. Comparison of leaching profiles amoung the three material types led to the conclusion that mercury-amended commercial calcium sulfate displays a different mercury release mechanism than the other two materials, and thus could not be used as a surrogate for FGD gypsum in the tests.

Researchers concluded that mercury in FGD gypsum was probably not a distinct mercury compound but tightly associated with the calcium sulfate matrix. Note that this is in contradiction with the NETL in-house research (presented later in the paper) that suggests mercury binds primarily with iron compounds available in the FGD gypsum. Another conclusion was that assuming a maximum temperature at the disposal site of 140°F, no mercury would evolve from disposed FGD materials. At a wallboard drying temperature of 400°F, some mercury was shown to evolve, but reduction of the temperature to 380°F was predicted to prevent mercury desorption.

Fate of Mercury in Synthetic Gypsum Used for Wallboard Production

USG Corporation is conducting mercury measurements at several full-scale commercial wallboard plants with the objective of determining whether any mercury is released into the

atmosphere when the synthetic FGD gypsum material is used as a feedstock for wallboard production.[35] Figure 14 presents a general schematic of the wallboard production process. Testing is being conducted using FGD gypsum from five different power plant/FGD feedstock variations to investigate the impact of different configurations on the stability of mercury during wallboard production. A summary of results is presented in Table 16.

Figure 14 – General Schematic of the Wallboard Production Process.[35]

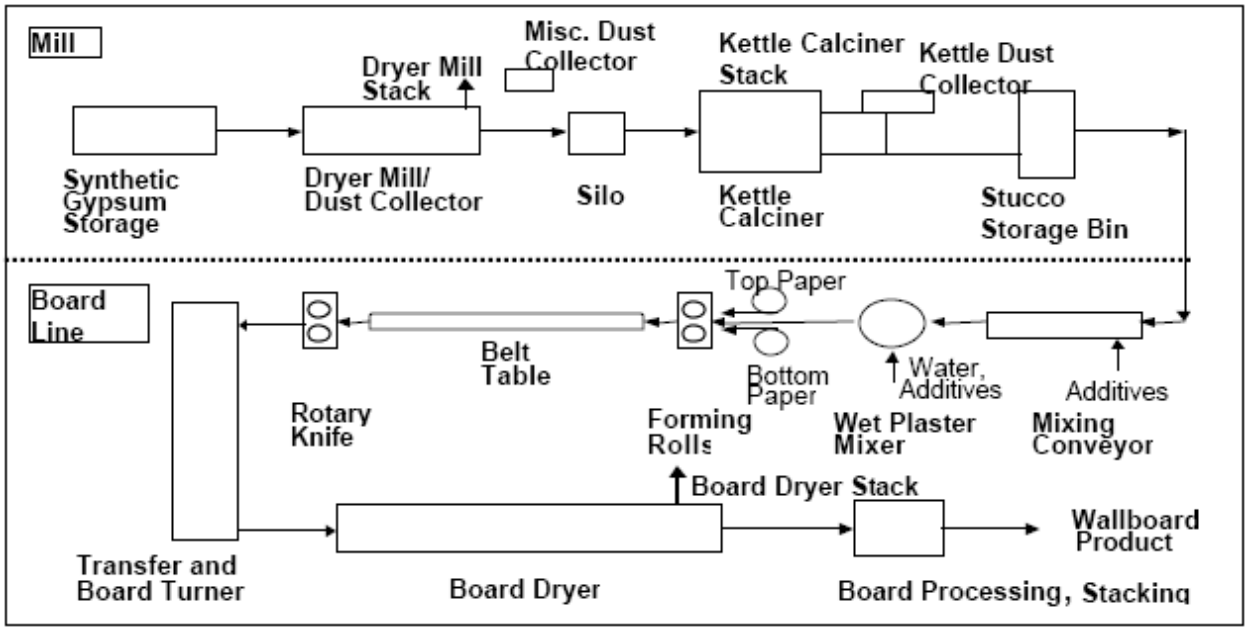


Table 16 – Results Summary for First Four Plant Configurations[35]

Site #	Coal Type	FGD	Fines Blowdown?	SCR?	Stack Hg Loss	Total Hg Loss	% Hg^0 in Stack
1	Bituminous	LSFO	No	Yes	5%	5%	90%
2	Bituminous	LSFO	No	No	3%	8%	90%
3	Bituminous	LSFO	Yes	No	42%	46%	99%
4	Lignite	LSFO	No	No	2%	2%	Not reported
5	Bituminous	LSFO	Yes	No	51%	51%	Not reported

The first FGD gypsum tested was from a power plant firing high-sulfur bituminous coal using LSFO FGD, no gypsum fines blowdown, and an active SCR. OH measurements detected only 1 to 2% of the mercury content being evolved from any one process vent stack with a total mercury loss across the wallboard plant of 5% of the incoming FGD gypsum mercury content. However, analysis of process samples indicated only 2% mercury loss from the gypsum across the plant. Analysis also indicated that greater than 90% of the mercury detected during vent stack testing was elemental mercury.

FGD gypsum from a power plant firing high-sulfur bituminous coal with LSFO FGD, no gypsum fines blowdown, and an inactive SCR system was used for the second set of tests. OH

measurements detected 0.3% mercury loss from the raw gypsum dryer mill stack and 2.6% loss from the gypsum calciner stack. Process samples collected across the wallboard product dryer kiln indicated an additional 5% mercury loss for a total of 8% mercury loss across the wallboard plant. Approximately 90% of the mercury detected by stack testing was elemental mercury.

The third FGD gypsum tested was from a power plant firing high-sulfur bituminous coal using LSFO FGD with gypsum fines blowdown and an active SCR. OH measurements detected 42% mercury emission in the mill portion of wallboard production with 1% loss across the dry mill and 41% loss across the kettle calciner. Solids analysis indicated an additional 4% loss across the board dry kiln, for a total estimated mercury loss of 46%. While the percentage of mercury emissions is significantly higher than other configurations tested, the gypsum tested in the third configuration had relatively low concentrations of mercury. The amount of mercury released from the third configuration was not much greater than other configurations when expressed on a mass basis. Analysis indicated that approximately 99% of the mercury detected during stack testing was elemental mercury.

FGD gypsum from a power plant firing Texas lignite with a dual-loop LSFO FGD, no gypsum fines blowdown, and no SCR system was used for the fourth set of tests. OH measurements detected less than 2% mercury emission during wallboard production (less than 1% each across the dryer mill, kettle calciner, and board dryer kiln). Emissions for this configuration were lower than for previous configurations (which all fired bituminous coal) on both a percentage and a mass basis. Most of the mercury detected by stack testing was elemental mercury.

The fifth FGD gypsum tested was from a bituminous plant using *ex situ* lime FGD, gypsum fines blowdown, and the SCR was bypassed. OH measurements indicated that 51% of incoming mercury in the FGD gypsum was emitted during wallboard production. The largest loss was about 50% across the calciner, with the remaining 1% lost across the wet gypsum dryer and product wallboard dryer.

Characterization and Management of Mercury in FGD By-Products

NETL's Office of Research and Development is conducting an in-house research effort directed at characterizing the fate of mercury in FGD materials.[36] This activity focuses on four topics: mercury stability during FGD gypsum drying; mercury stability during wallboard production using FGD gypsum; mercury leachability from FGD gypsum; and the mercury-binding phase in FGD gypsum.

Mercury stability during FGD gypsum drying was studied by analyzing FGD gypsum samples before and after use of a natural gas-fired dryer that reduces the moisture content of the FGD solids for ease of handling during the wallboard manufacturing process. Results from the analysis of grab samples taken before and after drying are presented in Table 17. Results indicate that within analytical precision, no mercury was lost during the drying, which is consistent with previous studies indicating that little or no mercury is released from FGD gypsum at temperatures below 170°F.

Table 17 – Mercury Stability During FGD-Gypsum Moisture Reduction.[36]

Hg and moisture analysis	Before drier		After drier	
	Sample 1	Sample 2	Sample 1	Sample 2
As-received Hg (µg/kg)	140 ± 6	142 ± 6	151 ± 2	158 ± 9
As-received moisture (%)	29.9	30.3	24.6	24.9
Hg, dry basis (µg/kg)	200 ± 8	204 ± 8	200 ± 3	211 ± 11
Hg, 2-sample average (µg/kg)	202 ± 8		205 ± 10	

Analysis of the stability of mercury in FGD gypsum during wallboard production was achieved by analyzing samples of FGD gypsum feedstock and samples from corresponding wallboard products from five wallboard manufacturing plants. Results of this analysis are presented in Table 18. The amount of mercury retained during manufacturing varied among the plants with plants A, C, and D showing high or complete mercury retention during the manufacturing process. Plant E displayed some moderate mercury release while plant B showed the most significant losses. It is suggested that the amount and thermal stability of mercury in gypsum and wallboard depend on the origin of the gypsum and/or the nature of the processing.

Table 18 – Mercury Retention During Manufacture of Wallboard from FGD Gypsum.[36]

	Plant A	Plant B	Plant C	Plant D	Plant E
Feed FGD-derived gypsum (µg/kg)	143 ± 4	251 ± 7	1221 ± 51	1464 ± 50	494 ± 16
Product FGD-derived wallboard (µg/kg)	147 ± 2	106 ± 5	1278 ± 63	1370 ± 59	421 ± 3
Hg retained during processing (%)	103 ± 3	42 ± 2	104 ± 7	94 ± 5	88 ± 3

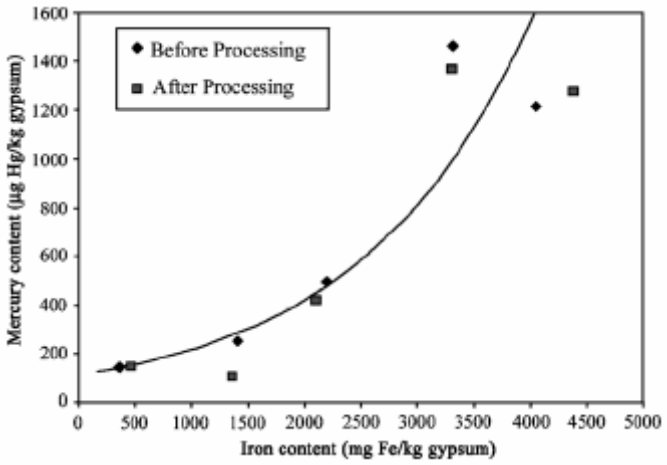
FGD by-product leaching studies are being conducted in a continuous, stirred-tank extractor (CSTX). Continuous stirring provides constant mixing as occurs in more traditional batch-leaching tests while continuous flow provides data over a wide range of pH values and liquid/solid ratios such as those seen in column leaching studies. Exhaustive leaching of the FGD gypsum in the tank has been found to remove essentially all of the gypsum and to leave behind an iron and aluminum rich insoluble residue that appears to be the phase responsible for Mercury retention in most samples. Researchers have found little mercury is emitted during leaching.

Results of metals analyses of the products presented in Table 18, settling experiments performed on FGD slurry samples, and leaching experiments all led to the conclusion that mercury binds primarily with iron in FGD gypsum. Metals analysis results are presented in Figure 15, showing the general correlation between iron and mercury contents. Settling experiments found mercury to be most concentrated in the top, slower-settling layer of the slurry. The top layer was also enriched with several metals, including iron. Leaching tests on FGD gypsum and wallboard did not mobilize the mercury. This is indicative of a strong chemisorption rather than physical

adsorption of mercury. Based on all of these results, it was postulated that an iron-containing phase was associated with the mercury sequestered in FGD gypsum.

NETL's In-house research is continuing in this area in order to better understand the association of mercury in FGD materials and to develop, as needed, management strategies that would prevent release of mercury to the environment from FGD materials.

Figure 15 – Correlation between Iron and Mercury Concentrations in FGD Gypsum and Wallboard.[36]



CONCLUSIONS

Questions related to the speciation, removal, re-emission, and potential re-release of mercury throughout the entire coal combustion process and the ultimate fate of mercury in resultant by-products need to be answered to provide accurate information regarding future regulatory decisions and to develop strategies and technologies to deal with mercury concerns. Issues of primary interest to the topic of *Mercury Capture and Fate Using Wet FGD at Coal-Fired Power Plants* are: (1) mercury oxidation by SCR; (2) mercury oxidation by other methods; (3) mercury capture and re-emission reduction by FGD; and (4) the fate of mercury in FGD by-products. NETL sponsored research is increasing the knowledge and understanding of these issues through field testing and technology development. An overview of the knowledge gained regarding each issue is presented below.

Mercury Oxidation by SCR, Individual Project Conclusions

- The increase in mercury oxidation across SCR systems when firing Eastern bituminous and PRB coals was examined. The amount of oxidation varied, with percentage point increases ranging from 10% to 71%. Variations were possibly due to differences in coal properties, catalyst design, and catalyst age. Oxidation of mercury is significant because FGD systems are more effective at removing oxidized mercury than elemental mercury. Based on the results of this particular set of tests on bituminous and PRB coals, average total mercury removal was 89% and 48% with and without SCR operation respectively.

- A 60% PRB and 40% mid-sulfur Eastern bituminous coal blend was demonstrated to have a 40% elemental mercury content at the SCR inlet which was reduced to <1% by the SCR outlet. Researchers reported that the blending of 60% PRB with the bituminous coal did not impact the oxidation potential of the SCR.

- The use of SCR and other APCD when burning bituminous coal was examined and the percent of oxidized mercury was found to be higher when an SCR was in-service with an average of 96% oxidized with SCR and 89.7% without SCR. Researchers indicated that the FGD system removed the same *percent* of oxidized mercury whether or not the SCR was used, but higher *concentrations* of mercury were removed by the FGD unit when using SCR.

- A global kinetic model of mercury oxidation across an SCR was developed to determine optimal catalyst properties and includes a wide variety of factors that can impact mercury oxidation. Analysis indicated that increasing chlorine content of flue gas was the recommended method for increasing mercury oxidation, though lowering the temperature was also found to increase oxidation. Additionally, mercury oxidation is higher when ammonia was not present.

Mercury Oxidation by Other Methods, Individual Project Conclusions

- Coal reburning was shown to result in flue gas consisting mainly of oxidized mercury and to have an efficiency of mercury removal at the ESP outlet that ranged from 6 to 40% when burning a blend of bituminous coals. FGD units are most effective at removing mercury that is in an oxidized form. The high levels of oxidized mercury achievable with the combustion modifications indicate a potential to combine this technology with FGD units to increase mercury removal rates.

- During testing at a North Dakota lignite-fired unit, the oxidized mercury concentration increased from 34% to 84% across the solid honeycomb Pd#1 catalyst.

- Initial evaluation of a variety of oxidation additives was conducted with SEA2 showing 44% removal without PAC and 50% or better with PAC.

Mercury Capture and Re-emission Reduction by FGD, Individual Project Conclusions

- Bench-scale testing and data evaluation suggests that sulfur complexes are major drivers for the chemical reduction of oxidized mercury to elemental mercury that can result in re-emission of mercury from the wet FGD absorber. Preliminary results indicate that low concentrations of chloride can slow the reduction of oxidized mercury to elemental mercury by sulfur, while high concentrations of chloride may completely inhibit the sulfur reactions, preventing the reduction of oxidized mercury to elemental mercury.

- Evaluation was completed of the use of a wet scrubbing mercury removal technology (which uses small amounts of liquid reagent) and found mercury removal rates across the

wet FGD system to range from 76% to 79% at one location using a limestone wet scrubber reagent with no signs of re-emission and 51% at a second location using a Thiosorbic® lime (magnesium enhanced lime) wet scrubber reagent with signs of re-emission. Researchers also found that mercury in the wet FGD slurry was associated with fines.

- Research into the use of TMT-15, an FGD additive, is being conducted, and initial results show a decrease in FGD liquor total mercury concentration during tests with the additive (from >20 µg/L without additive to approximately 5 µg/L with TMT-15). Pilot-scale tests to determine the effectiveness of TMT-15 at preventing mercury re-emission were inconclusive due to a lack of re-emission during operation without the additive. Researchers indicated that most of the mercury appeared to be associated with the FGD fines. Full-scale testing is now in progress

- While studying the effects of SCR operation on mercury oxidation levels, researchers found elemental mercury concentrations to increase across the wet FGD system for both cases with and without the SCR in operation, indicating re-emission of mercury across the wet FGD system.

Fate of Mercury in FGD By-Products, Individual Project Conclusions

- Research concluded that no mercury is evolved from disposed FGD by-products at temperatures of 140°F or less, but at the wallboard drying temperature of 400°F, some mercury emissions would be expected. Researchers predicted that a reduction of drying temperature to 380°F should prevent mercury emission. Researchers also concluded that mercury in FGD gypsum is probably associated with the calcium sulfate matrix.

- Characterization of mercury emissions during wallboard manufacturing using FGD gypsum from five different power plant configurations is currently on-going. Three configurations showed mercury emissions of 8% or less across the wallboard plant, while one configuration showed 46% emission (although the emissions on a mass basis were not much greater than other configurations). In all configurations, most of the mercury emitted during stack testing was found to be elemental mercury (90% or greater).

- Researchers found no release of mercury during FGD gypsum drying to reduce moisture content. Researchers analyzed FGD gypsum feed and resulting wallboard products from five wallboard manufacturing plants and found three plants with high or nearly complete mercury retention, one plant with a mercury retention of approximately 88% and a fifth plant with a retention rate of only 42%. Researchers also analyzed FGD gypsum and wallboard and determined that mercury is most likely bound to an iron complex in the FGD gypsum.

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