Factors Affecting Mercury Chemistry and Capture in Wet FGD Systems

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Presentation Outline

- Background on mercury (Hg) capture by wet FGD
- Hg oxidation technologies to enhance FGD capture
- Understanding and controlling Hg reactions in wet FGD systems
- Hg effects on FGD byproducts

Acknowledgement

Unless otherwise noted, data presented in this presentation are from current URS projects being conducted with funding from U.S. DOE-NETL, EPRI, USG Corporation, and a number of individual utilities

Background on Wet FGD Capture of Mercury (Hg)

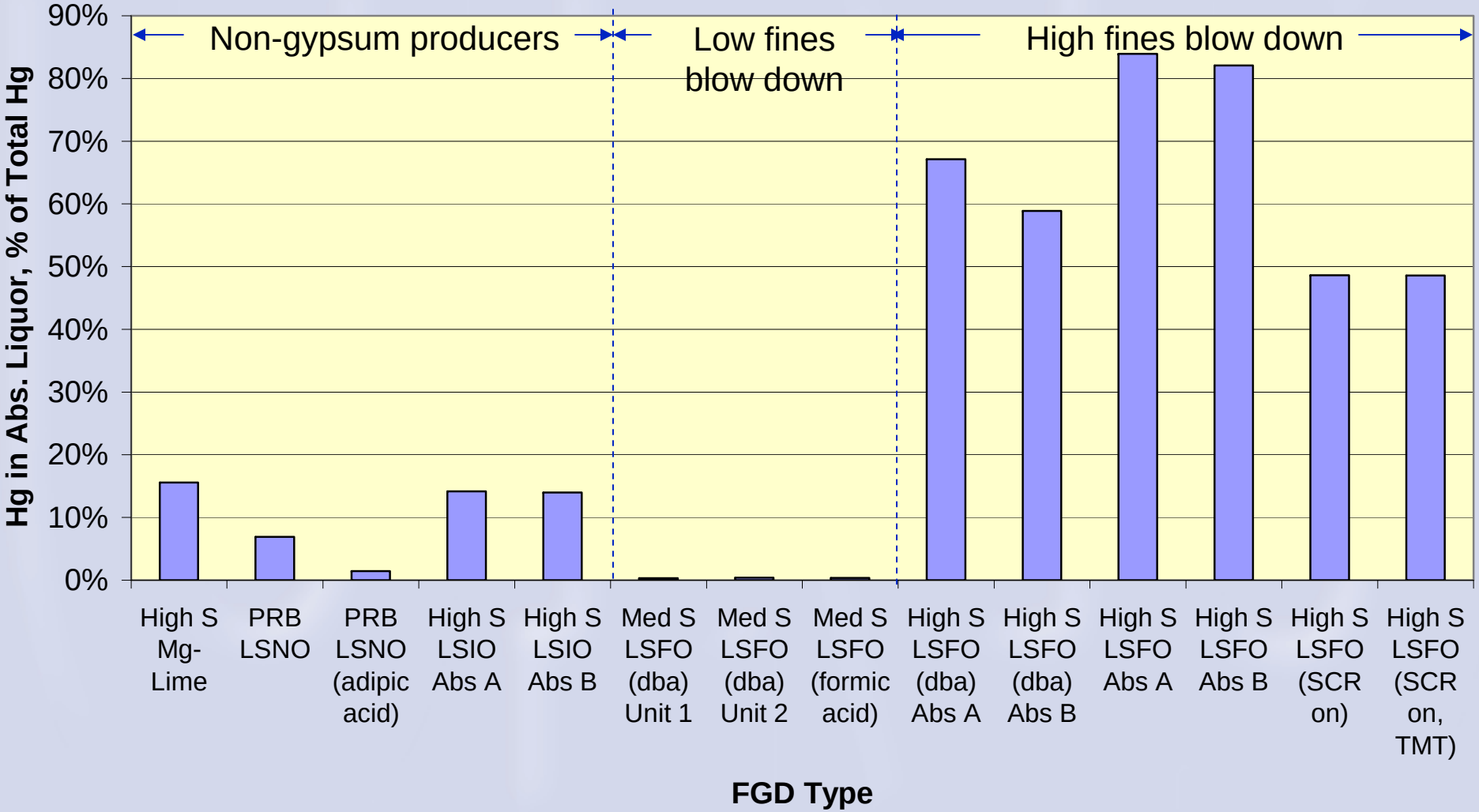
Hg Capture by Wet FGD

- Downstream of ESP or baghouse, Hg in flue gas is a mixture of elemental (Hg^0) and oxidized forms (Hg^{+2})
  - Hg oxidation is strongly influenced by Cl in coal
- Hg^{+2} is very soluble in aqueous solutions, but Hg^0 is relatively insoluble
- Hg^{+2} can be absorbed at high efficiency by wet FGD absorbers, Hg^0 is not
- In theory, nearly all of the Hg^{+2} should be removed by the FGD, and stay in the liquor

Field Observations of Hg Capture by Wet FGD – Can Differ from Theory

- Net capture of Hg^{+2} can be limited by "re-emissions"
  - Evidence is seen when Hg^0 conc. is higher at FGD outlet than at inlet
  - Overall reaction is believed to be:
    $Hg^{2+} + HSO_3^- + H_2O \rightarrow Hg^0\uparrow + SO_4^{2-} + 3\ H^+$
- Hg is often found predominantly in FGD solids
  - Mechanism not well understood
  - May be due to adsorption on impurities
  - Hg tends to be concentrated in fine particles

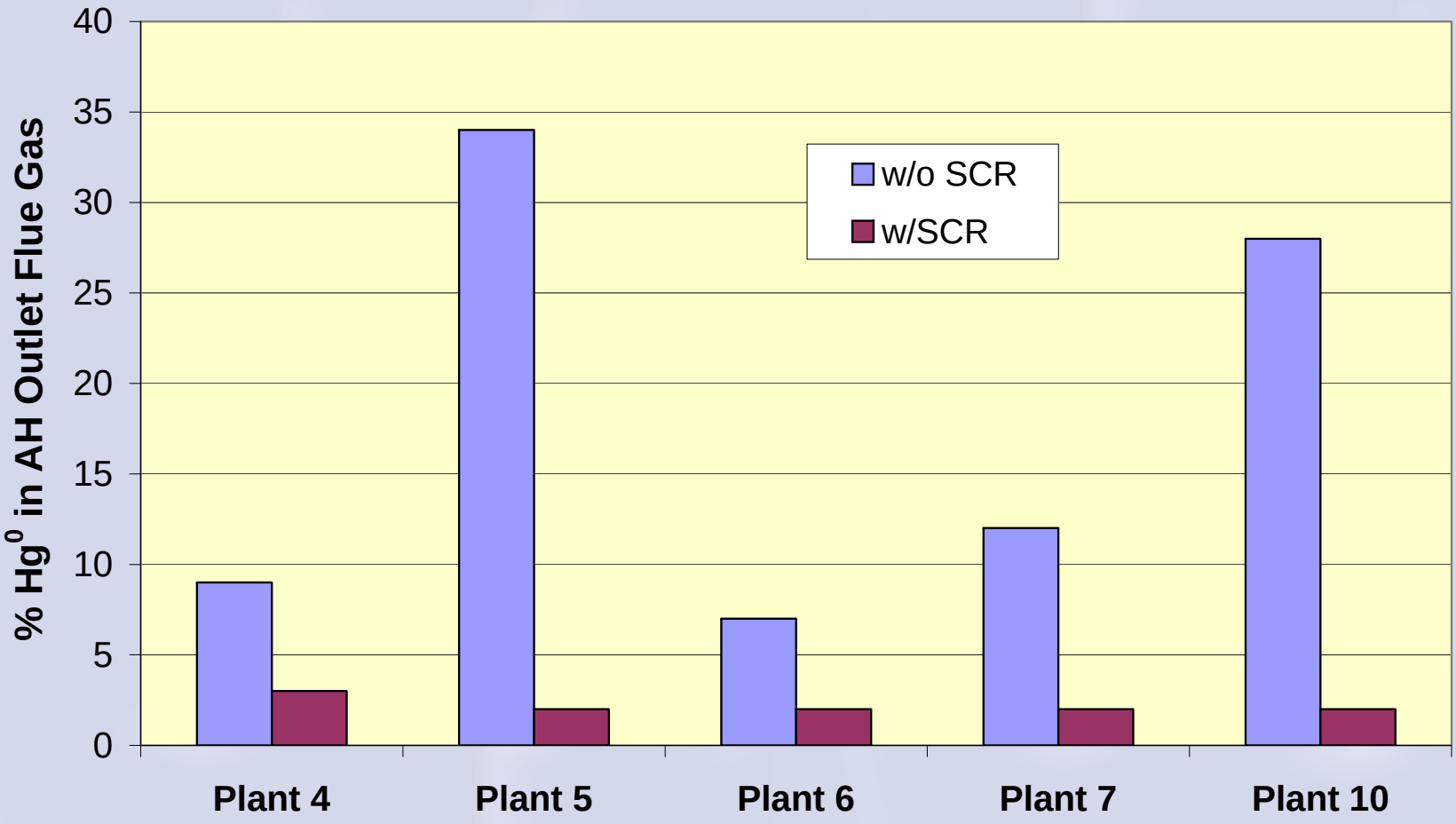
EPRI Data: Absorber Recycle Slurry, % of Hg in Liquor – What Controls?



Role of FGD in Meeting CAMR

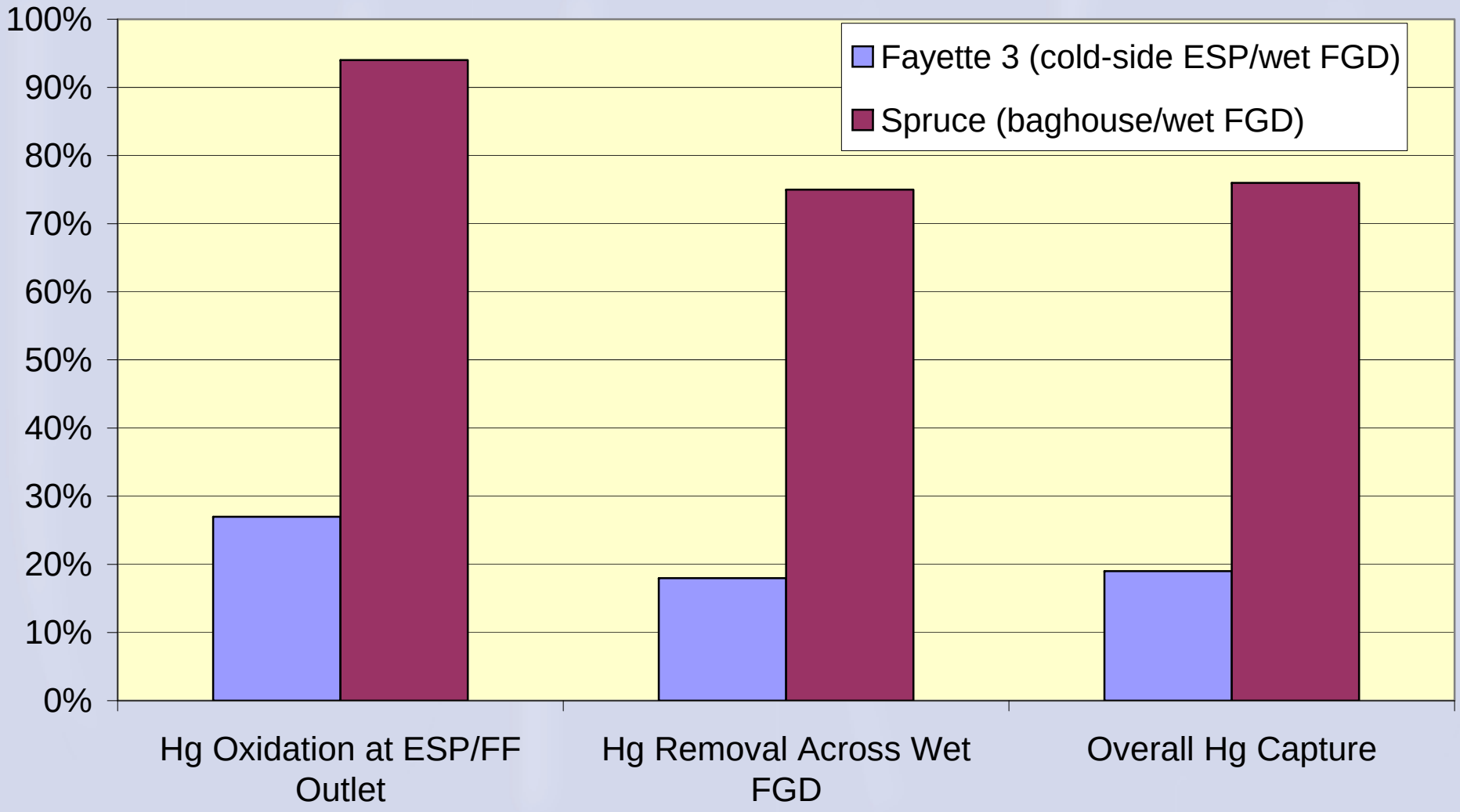
- EPA expects 2010 Hg limits to be met largely by co-benefit of FGD retrofits to meet CAIR requirements
  - SCR retrofits on bituminous coals can enhance oxidation of Hg, capture by wet FGD
  - Baghouses for particulate control also enhance oxidation and capture
- Other technologies are under development to enhance Hg oxidation at FGD inlet
  - SCR catalysts optimized for FGD oxidation
  - Low temperature Hg oxidation catalysts
  - Injection of halogens with coal

Effect of SCR on Hg Oxidation (Bituminous Coals)*

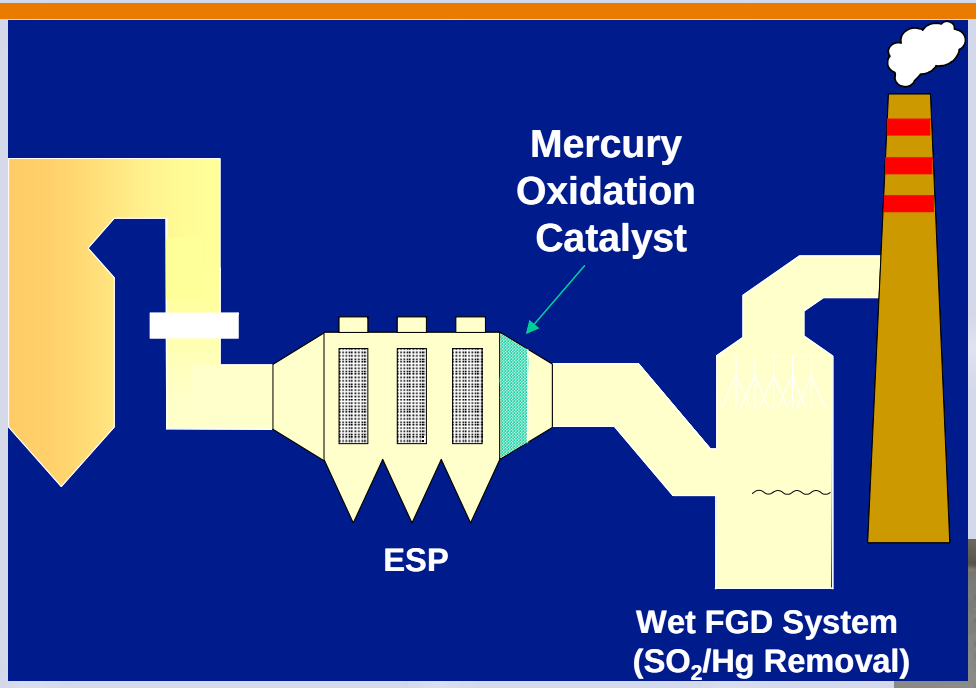


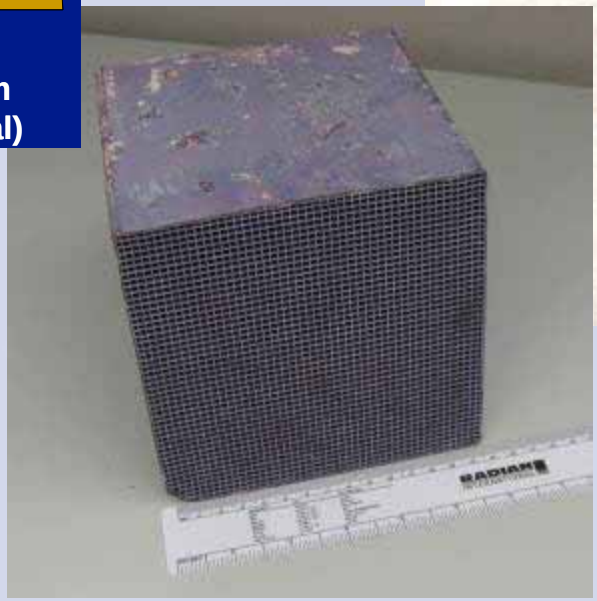
*Source: Consol/DOE-NETL

Effect of Baghouse vs. ESP for Particulate Control – PRB Coal



Hg Oxidation Catalysts



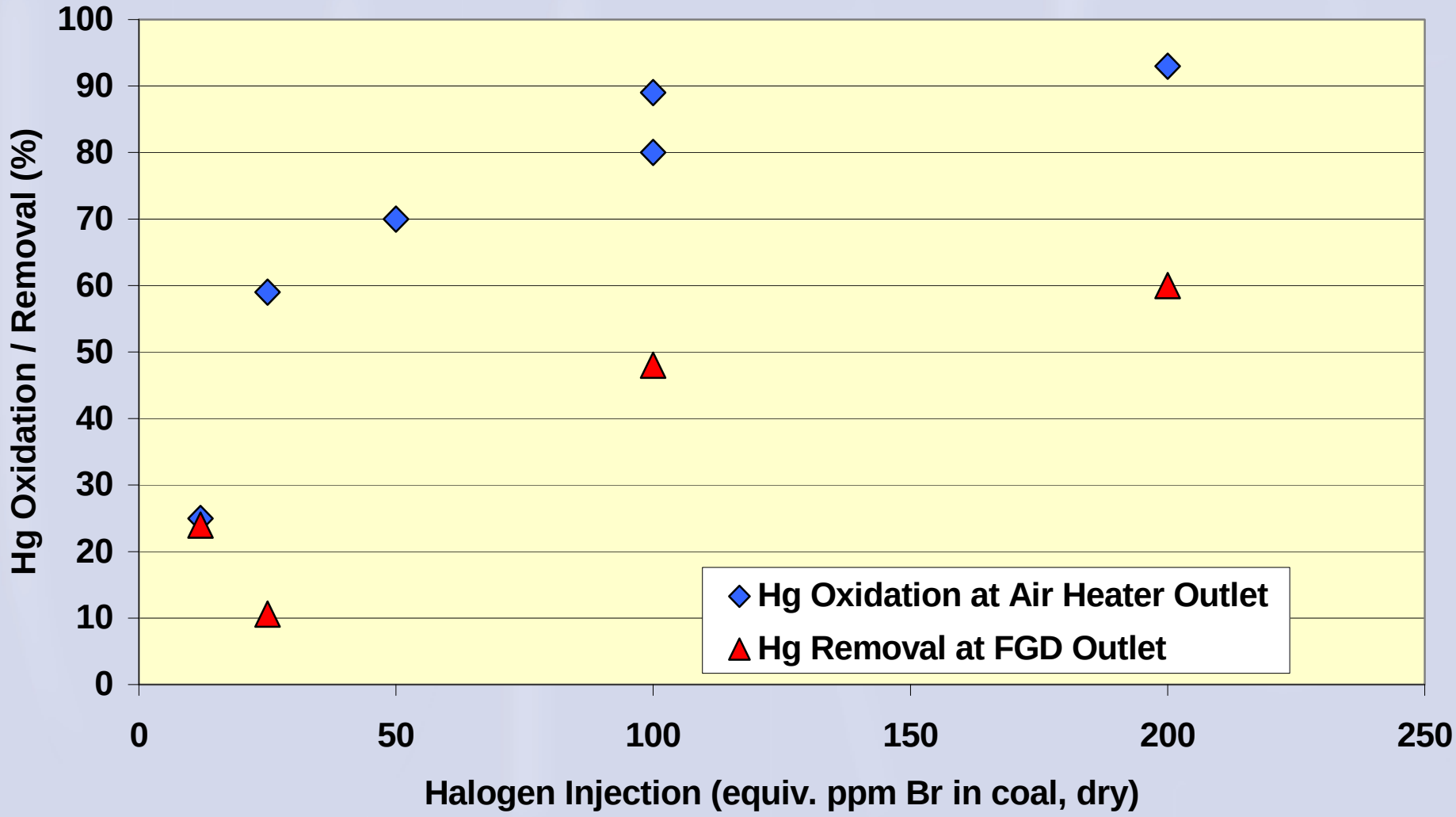


200 MW demonstration of this technology to be conducted at LCRA Fayette Power Project starting April 2008

Halogen Injection for Hg Oxidation

- **Add solid salt to the coal**
- **Spray salt solution into coal**
- **Bromide more effective than chloride**
  - **Patented by Vosteen Consulting**
  - **Licensed by Alstom in US (KNX)**

Halogen Injection Into Furnace – Effect of $CaBr_2$ on plant firing Lignite/PRB blend

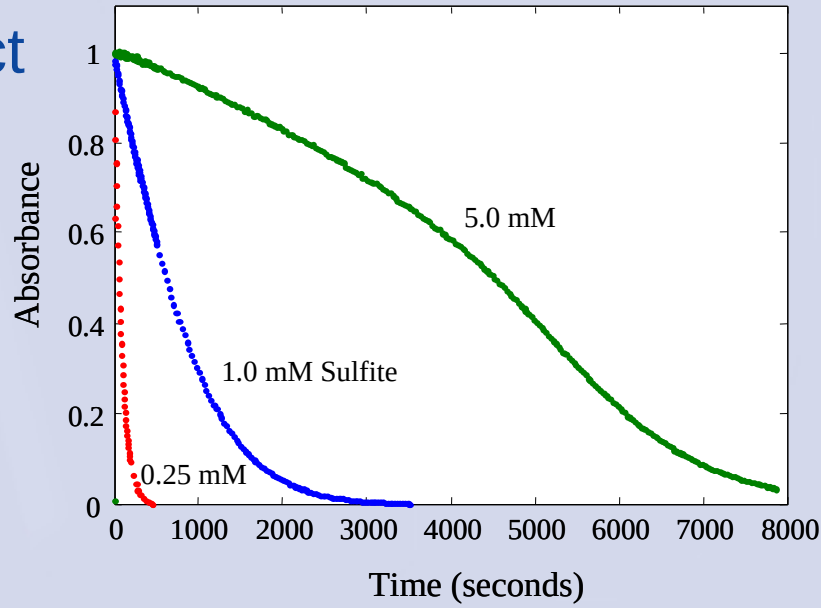


Understanding and Optimizing Hg Capture by Wet FGD

- Bench-scale evaluation of Hg reaction mechanisms and kinetics
  - Develop ability to predict FGD Hg re-emissions, optimize FGD conditions to minimize or eliminate
  - Secondary goal is to control whether Hg stays in FGD liquor or goes to solids
- Pilot- and full-scale tests of wet FGD additives
  - “Empirical” approach may accomplish same objectives

Chemical Reactions for Hg^0 Re-emission

- Overall reaction:
  - $Hg^{2+} + HSO_3^- + H_2O \rightarrow Hg^0\uparrow + SO_4^{2-} + 3\ H^+$
- Reaction mechanisms are complex
- Main pathways through mercuric-sulfite and chloro-mercuric-sulfite complexes
  - pH, sulfite, chloride levels impact re-emissions (low levels of all three favor re-emissions)
  - Need to better understand competing Hg adsorption on FGD fines (Hg on solids does not re-emit

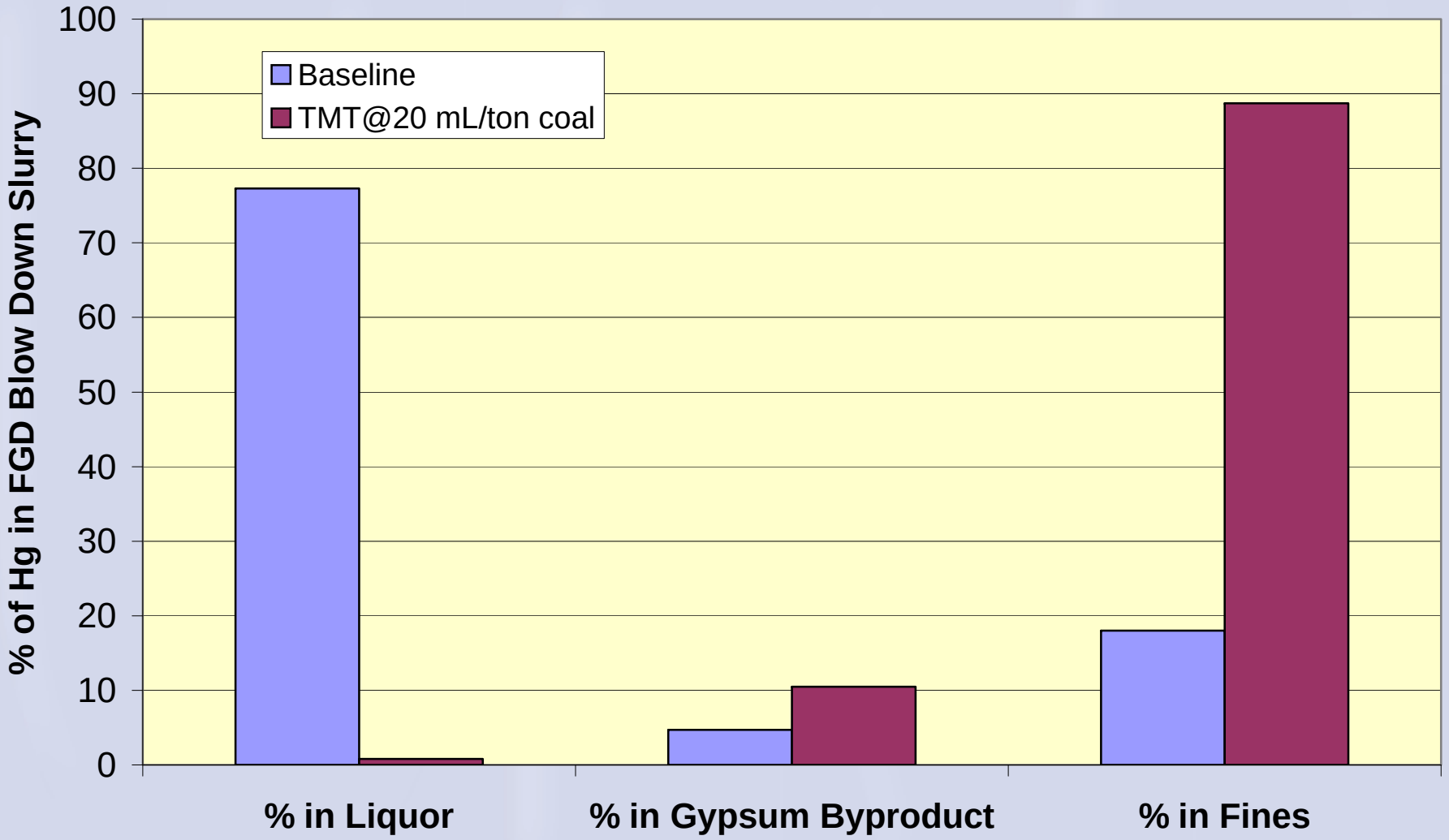


Wet FGD Additives

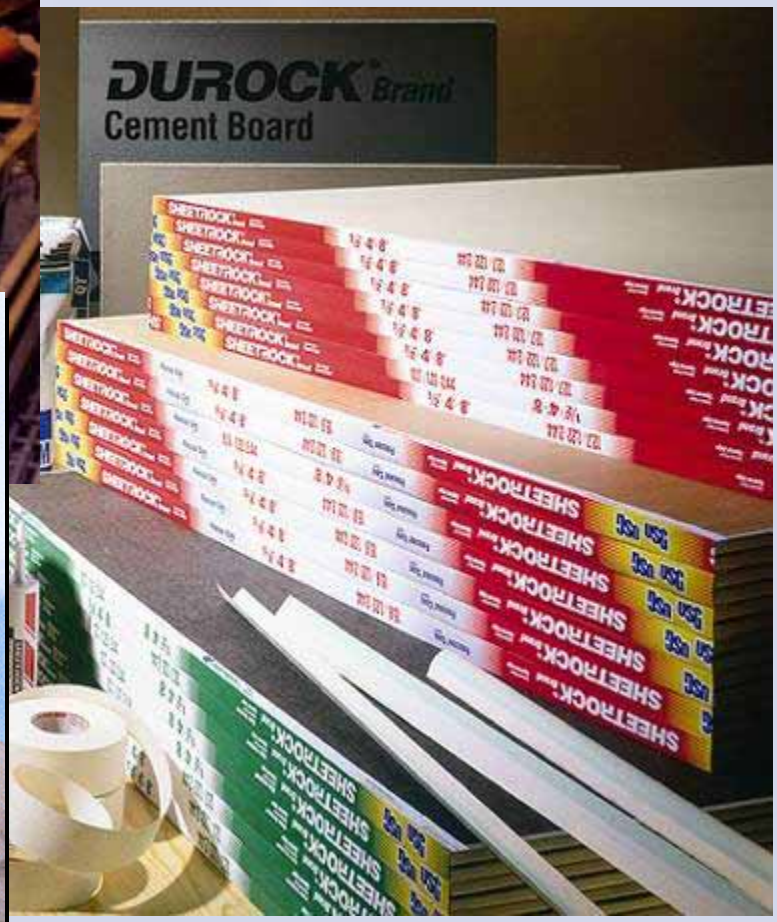
- Intended to precipitate Hg^{+2} before it can undergo re-emission reactions
- Most contain sulfide functional groups
- Typical additives:
  - TMT-15 (Degussa)
  - Nalco
  - Sodium hydrosulfide (B&W)
  - Solucorp
  - PRAVO (Vosteen Consulting)

- Effectiveness in full-scale trials varies – more work is needed

Effect of TMT on Hg Distribution in FGD Slurry

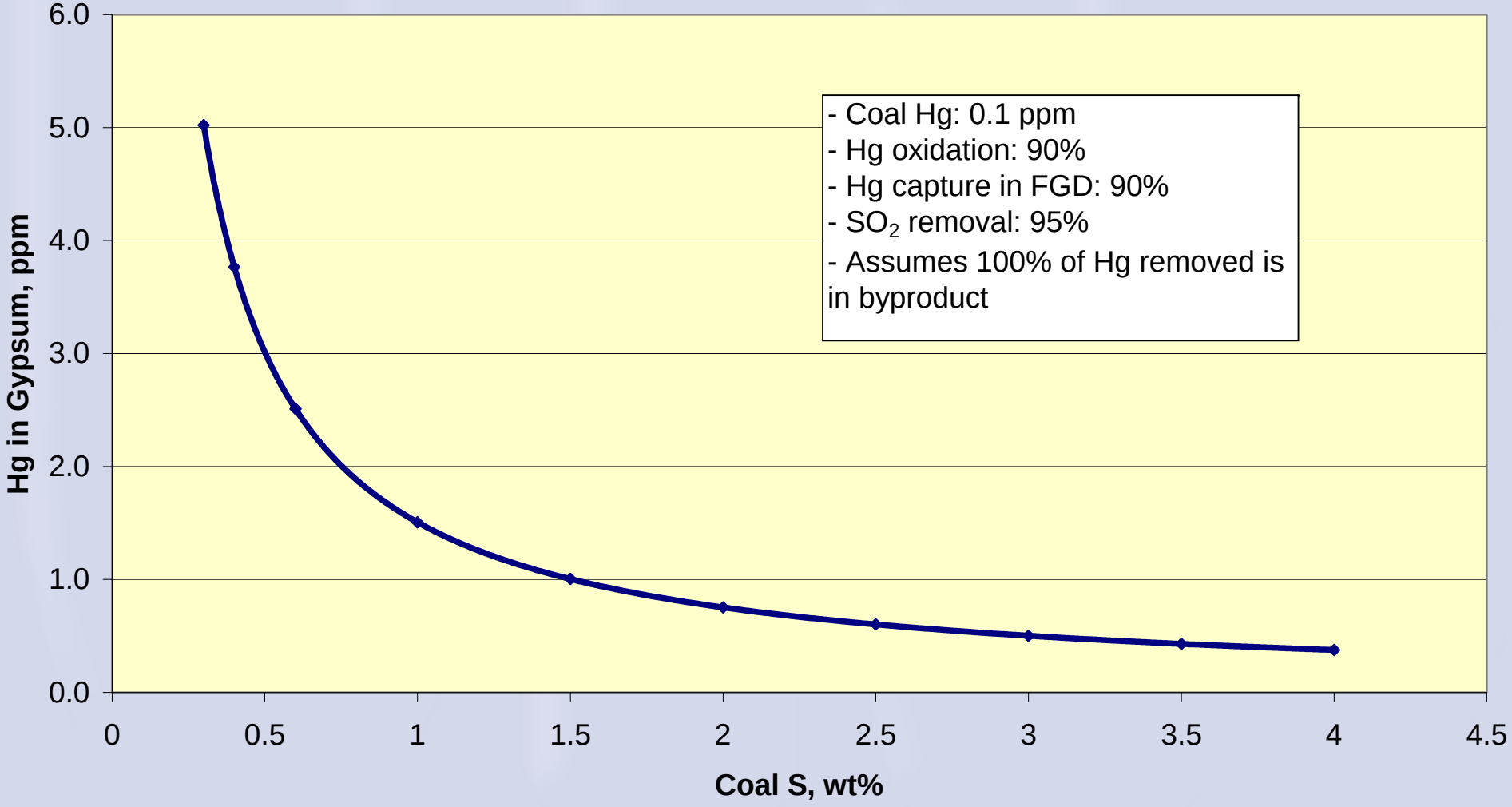


Effects of Hg Removal on FGD Gypsum



Effects of Hg Oxidation and FGD Capture on Hg in Gypsum

What happens to the mercury when you reuse FGD gypsum?



Natural vs. FGD Gypsum Hg Analyses*

Gypsum Source	Hg Concentration, ng/g (ppb)
Natural Gypsum	<4 – 26
FGD Gypsum	100 – 1100

*Results for 10 USG wallboard plant feedstocks each

Ongoing Project to Measure Hg Stability During Wallboard Production

- Project led by USG Corporation (project management, host sites, co-funding)
- Co-funding by DOE-NETL and EPRI
- Measure Hg losses when using FGD gypsum to produce wallboard
  - Seven different wallboard plant tests, representing a range of FGD gypsum sources
  - Results to be discussed in later presentation
- Measure Hg leaching stability in wallboard product

TCLP Results for Wallboard from FGD Gypsum

Sample	Hg (μg/L)
Task 1 - Power Plant A (w/SCR)	<0.25
Task 2 - Power Plant A (no SCR)	<0.25
Task 3 - Power Plant B (high fines BD)	<0.25
Task 4 - Power Plant C (Tx Lignite)	<0.25
Task 5 – Power Plant D (high fines BD)	<0.25
Task 6 – Power Plant D (w/TMT)	<0.25
Primary Drinking Water Standard	2
MCL per 40 CFR 261.24 (Haz. Waste)	200

Research Needs for Hg Capture by Wet FGD

- Complete kinetics model for Hg reactions in FGD
  - Control re-emissions
  - Control phase in which Hg leaves FGD
- Further demonstrate re-emission additives at full scale
- Determine FGD gypsum Hg losses in other calciner types (all results to date only for USG kettles)
- Determine what controls Hg partioning between solids and liquor, Hg losses from FGD gypsum in thermal processes
- Determine Hg stability in other FGD gypsum reuses (e.g., land application)