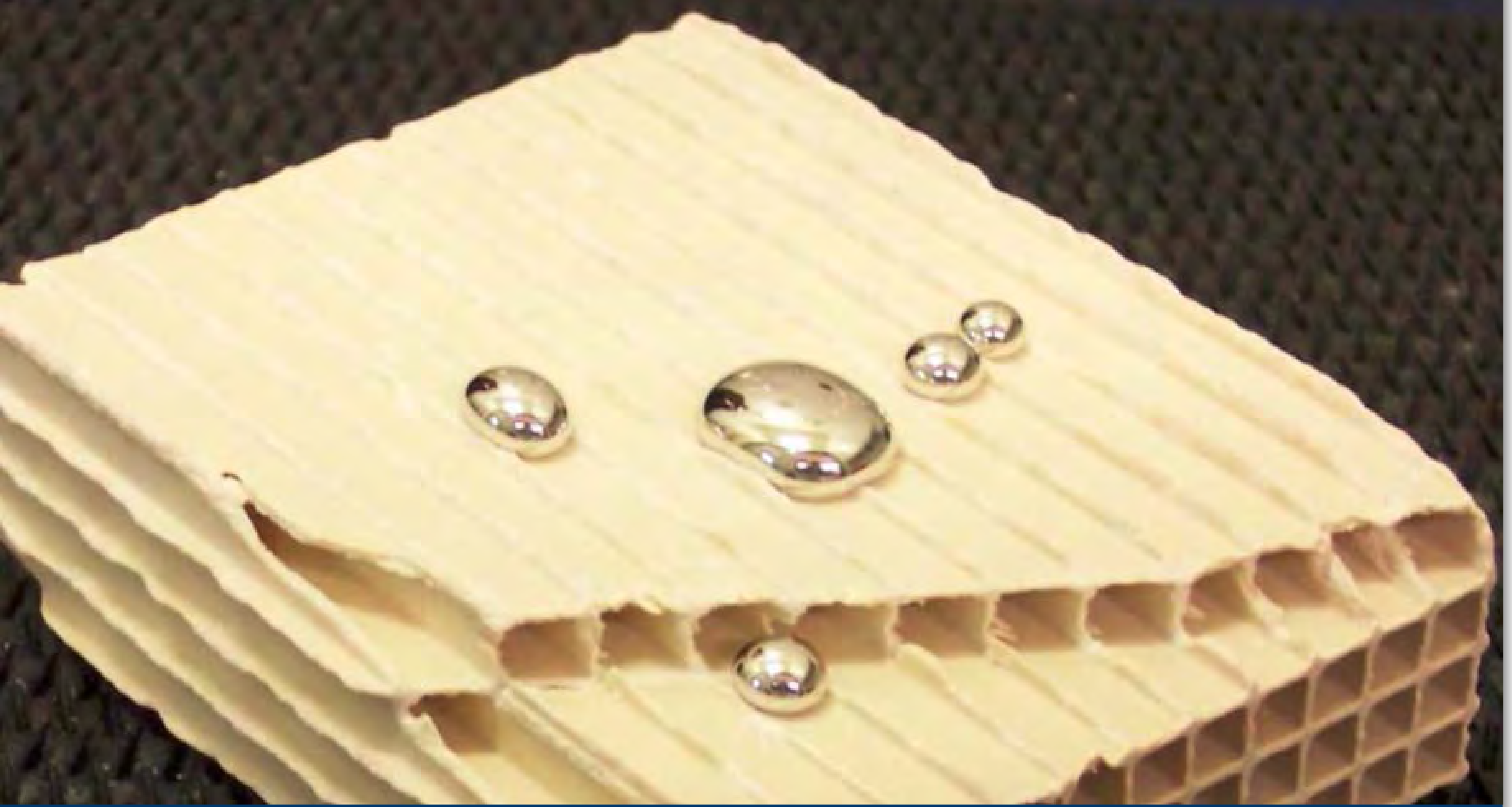
REINHOLD ENVIRONMENTAL Ltd.

2015 NOx-Combustion Round Table & Expo Presentations

February 23 & 24, 2015, in Richmond, VA / Hosted by Dominion



Part II: Perspectives on Mercury Oxidation Testing

Tom Weir (Duke Energy) and Thorsten Dux (STEAG)
Februrary 24th, 2015

Topics

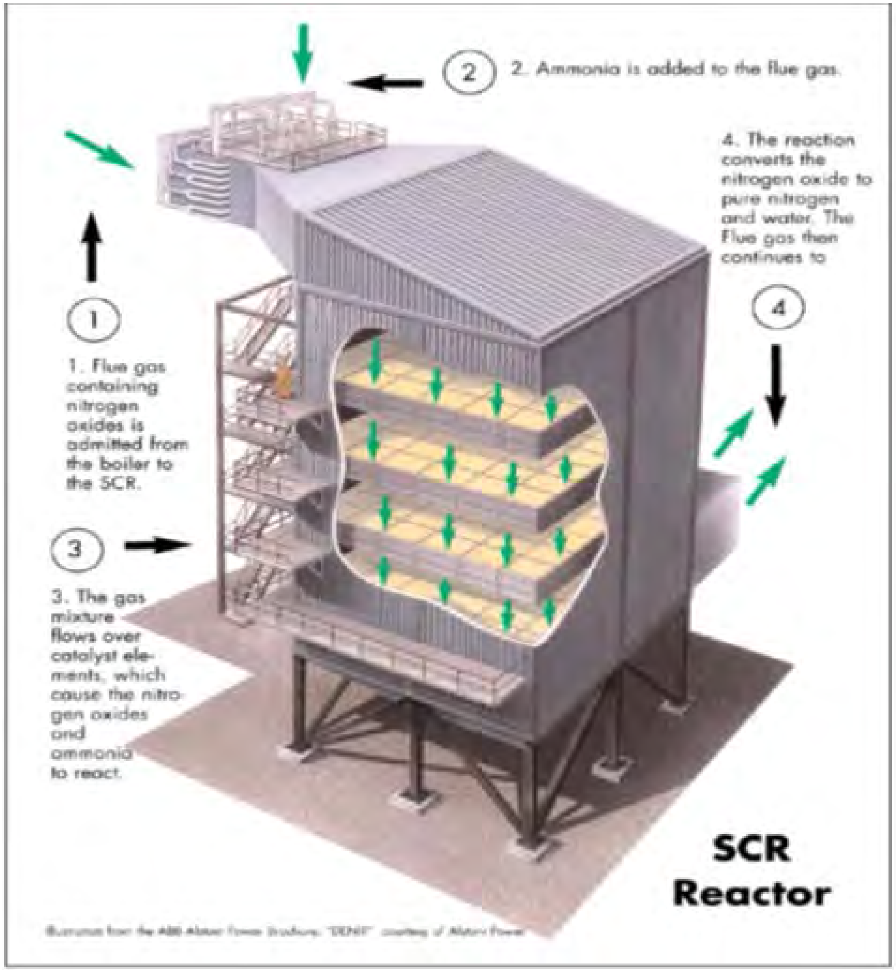
- Overview SCR
- Mercury Oxidation at the SCR
- Catalyst activity
- Mercury testing protocol
- Catalyst management

- How to control mercury
- Field Testing vs laboratory
- How to develop a protocol
- Next steps

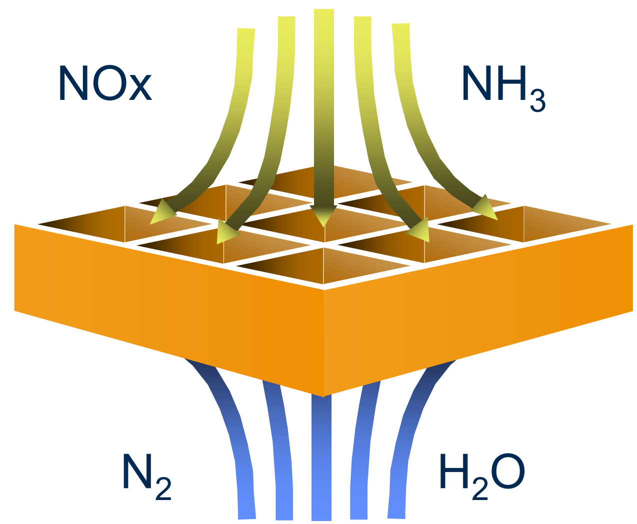
Mercury Emissions Compliance

- The Mercury and Air Toxics Standard (MATS) regulations that start in April 2015 include limits for mercury emissions.
- Some units have been granted a one year extension.
- Limit is a rolling 30 day average of 1.20 lb/TBtu for mercury (Hg) emissions. Also provisions for a 90 day facility average .
- **SCR's added purpose is to oxidize mercury such that it is in a water soluble state entering the scrubber.**
- Note that it takes both the SCR to oxidize the mercury and the scrubber to collect the oxidized mercury for mercury emissions out the stack to be reduced.

SCR Fundamentals – NOx Reduction



- **Originally designed to remove NOx**
- **NOx reacts with injected ammonia at the catalyst**



Mercury Oxidation Reactions

Mercury in the flue gas is a mixture of elemental and oxidized mercury

- **Formation of mercury oxide in the furnace**

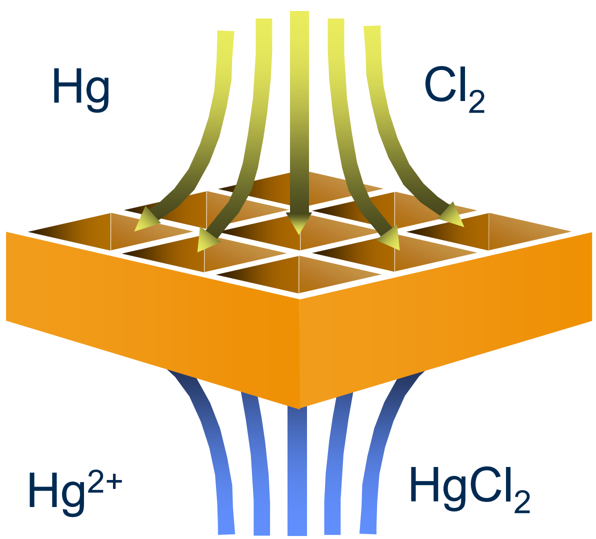
  $$2\ Hg + O_2 \rightleftarrows 2\ HgO$$

- **Formation of elemental halogen (i.e. chlorine, bromine, iodine) in the furnace**

  $$4\ HCl + O_2 \leftrightarrows 2\ H_2O + 2\ Cl_2$$

- **Oxidation of mercury (in the SCR with vanadium catalyst)**

  $$Hg + Cl_2 \rightleftarrows HgCl_2$$



Four SCR Mercury Oxidation Parameters

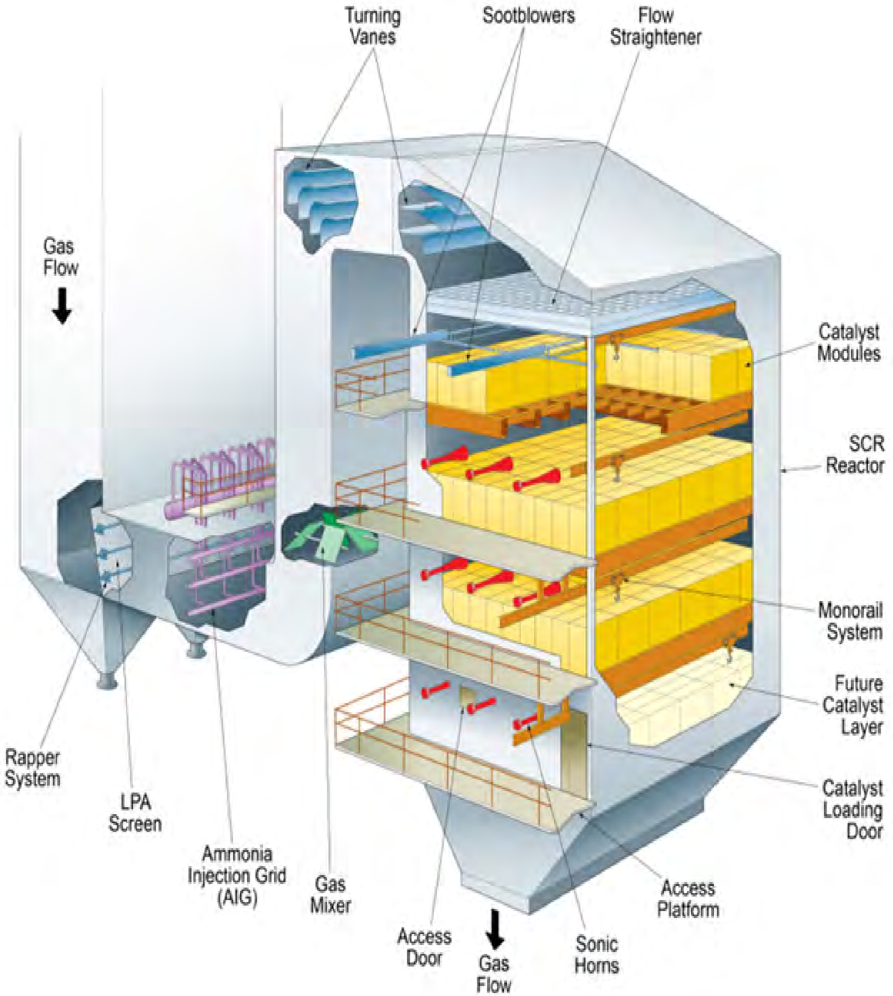
1) **Temperature:** Lower temperatures (620 to 680°F) better for Hg oxidation and minimizes SO_2 to SO_3 oxidation.

2) **Halogen content:** Sufficient halogen content is necessary for the Hg oxidation reaction to take place. Halogen can come from coal or additive such as i.e. $CaBr_2$.

3) **Ammonia Injection Rate:** NH_3-NOx reaction is preferential thus ammonia concentration in the flue gas strongly affects Hg oxidation.

4) **Total Catalyst Activity:** Must have sufficient catalyst activity to remove NOx and subsequently oxidize mercury.

Ammonia Injection Rate



- **The NOx reaction with NH_3 is preferential over the SO_2 and mercury oxidation reactions.**
- **Thus the majority of mercury oxidation takes place after all the ammonia has reacted with NOx.**
- **The more ammonia injected (for higher NOx removal) the less catalyst is left in the flue gas path to oxidize mercury (☺) or the more catalyst needs to be added for that purpose.**

Total Catalyst Activity

Current State – NOx Only Objective

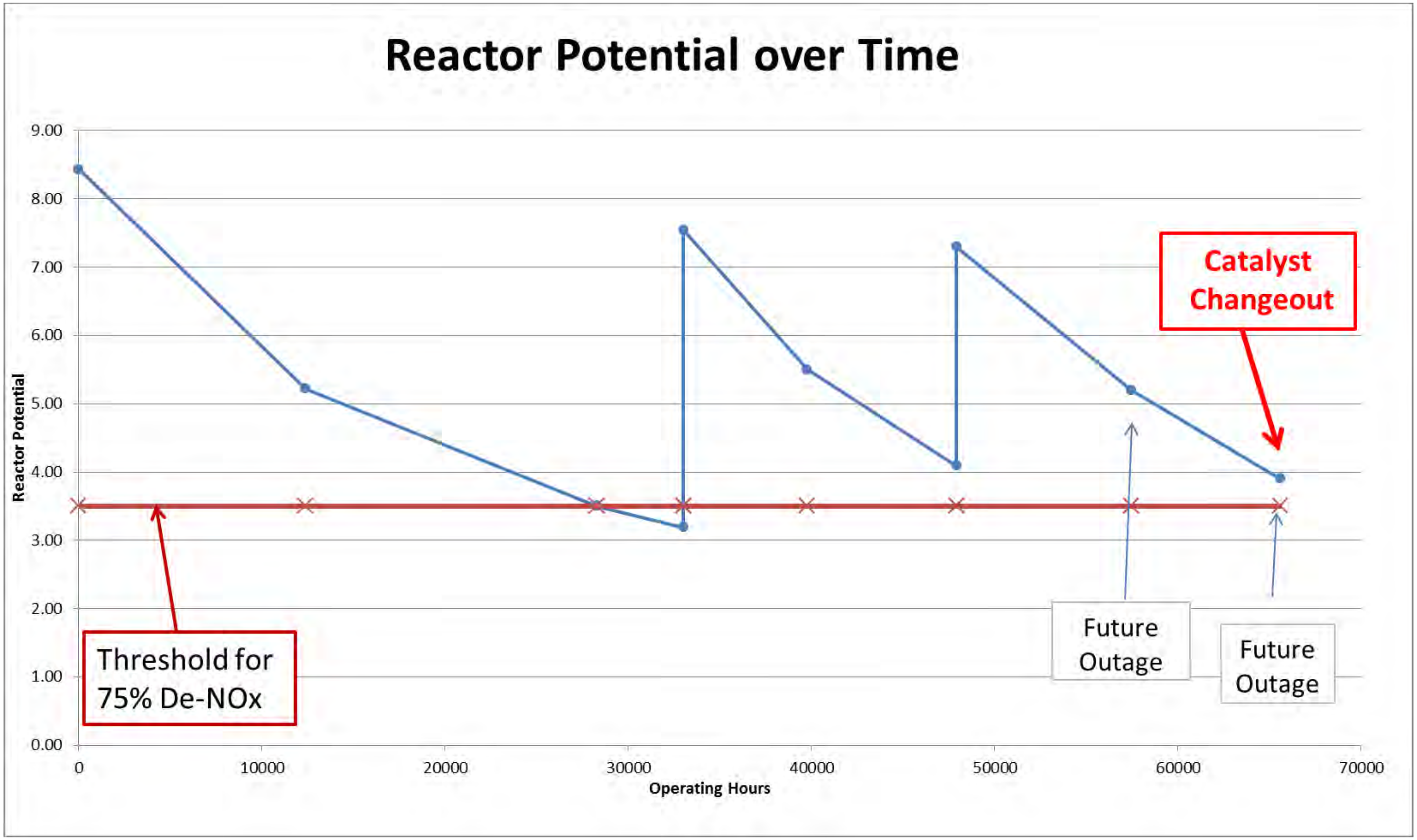
- Maintain adequate SCR reactor potential (K/AV) to meet DeNOx requirements based on NOx strategy.
- Make timely prediction of catalyst end-of-life.

NOx *and* Mercury Oxidation Co-Benefit Objectives

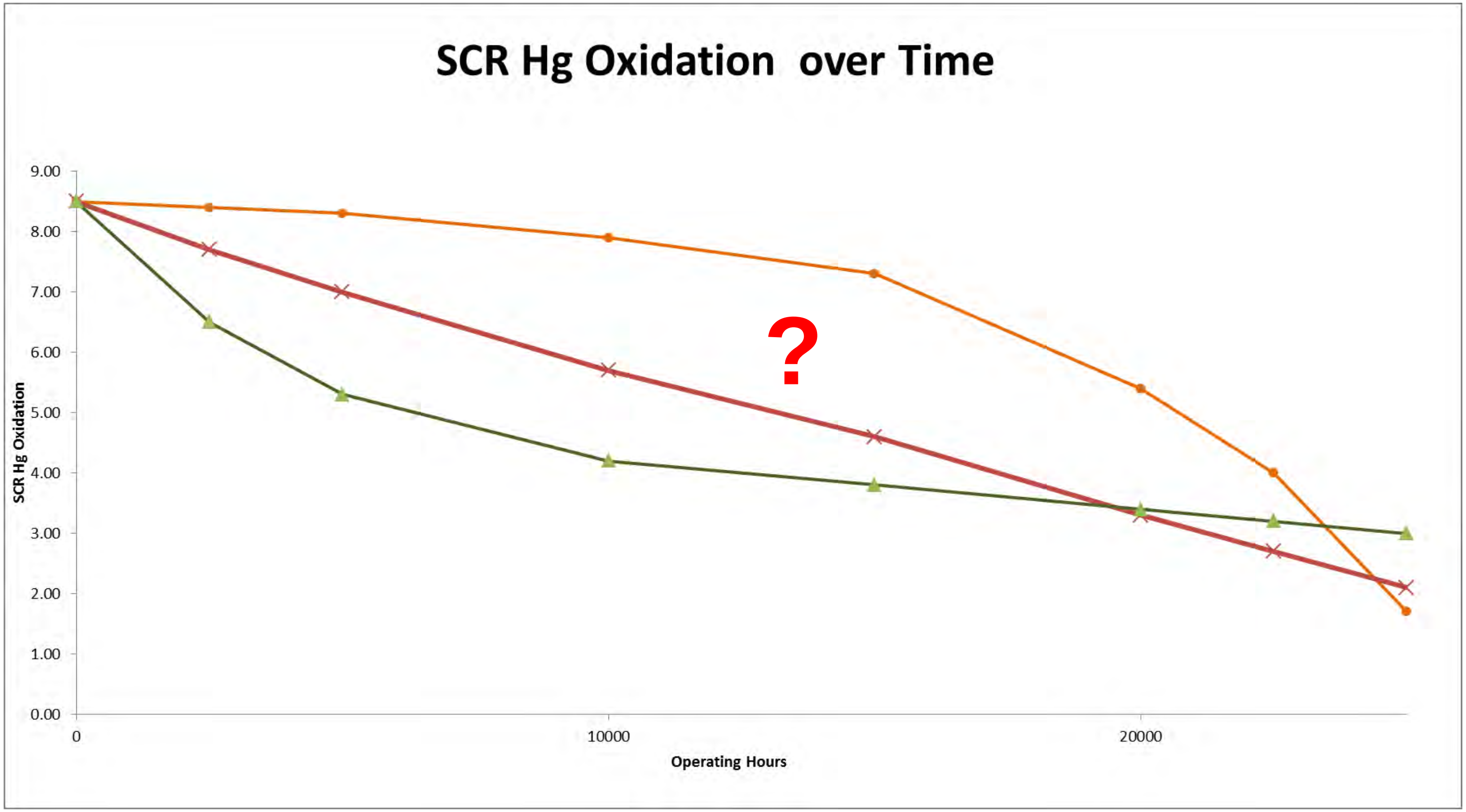
- Maintain adequate SCR reactor potential to meet DeNOx requirements based on NOx strategy .
- Maintain adequate SCR mercury oxidation capacity to meet goals based on overall mercury strategy.
- Make timely prediction of end-of-life based on NOx and Hg oxidation strategy – whichever is most restrictive.

Note that installing additional catalyst volume will meet above strategy, but will also increase SCR DP and increase SO2 to SO3 conversion.

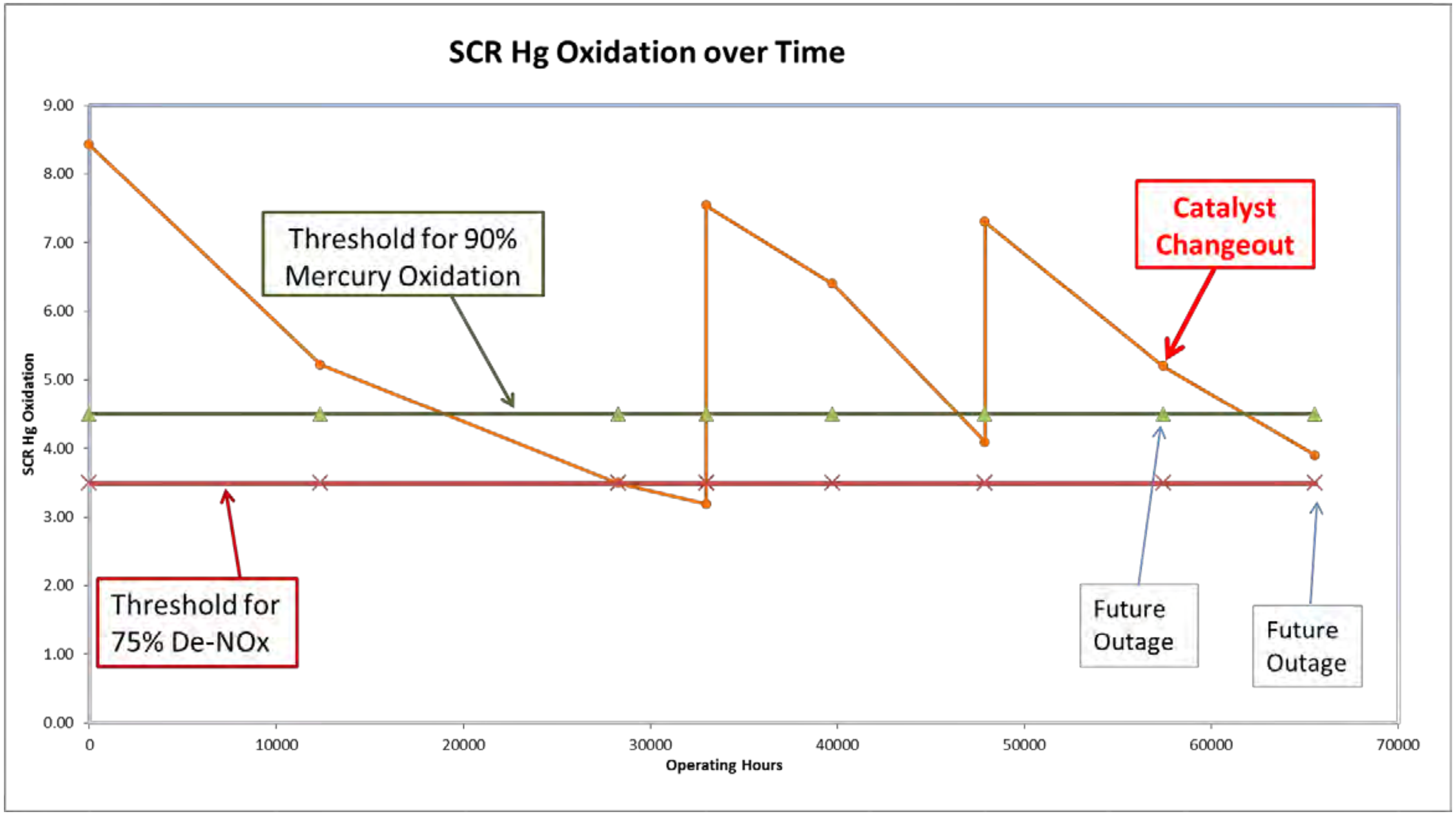
NOx Only Strategy



Mercury Oxidation Curve Shape??



NOx and Hg Strategy



The Utility Dilemma - Processes to predict SCR catalyst degradation of mercury oxidation are not yet well established.

Methods to Determine Catalyst Mercury Oxidation Condition

1) **Perform mercury speciation testing on the unit – pre and post SCR:**
   - A concern with field testing is the constantly variable and largely unknown flue gas composition at any given point in time
   - Measurement techniques are currently not proven,
   - EPRI will be working with Duke in 2^{nd} quarter to establish a proper sorbent trap measurement approach,
   - Can be done as stack CEMS indicates a performance drop-off,

2) **Develop mercury oxidation capacity charts utilizing catalyst sample testing:**
   - Concept would be to mirror current NOx catalyst management planning (CMP) methods .
   - Can be utilized to understand rate of catalyst performance drop off and proactively predict future performance.

Key CMP Input # 1: Percent Hg Oxidized

Perform yearly catalyst test for Hg oxidation:

- **Should be focused on "condition of catalyst".**
- **Not utilized (stand alone) to identify "How much Hg is being oxidized by the overall SCR" in absolute amounts.**
- **Should not be based on catalyst installed location (which layer).**
- **If the correct testing conditions are held constant, results from year to year are expected to be the condition of the catalyst – only, which allows plotting a mercury oxidation capacity degradation curve.**
- **Identifying the most suitable testing conditions is in progress – including work by EPRI.**

Key CMP Input # 2: Hg Oxidation Capacity

Understand how lab results will be utilized to predict field performance.

- **Needs to include a "set of other factors" such as:**
  - Coal to be burned
  - Catalyst location – which layer
  - Ammonia injection rate
  - Halogens to be added (through coal and/or separately)
- **This "set of layer by layer operational parameters" will collectively determine the SCR's overall contribution to the Hg oxidation strategy.**
- **This understanding will be more complex than NOx due to all the variable factors that will need to be considered in addition to "the condition of the catalyst".**
- **We may find out that catalyst condition for mercury oxidation is never(??) more restrictive than for NOx removal.**

Mercury Testing Protocol

- **A Mercury Oxidation Testing Protocol should define apparatus and standard conditions for lab testing of catalyst – similar to the NOx Testing Protocols by EPRI and VGB**
- **A key difference from the NOx testing protocol is that the gas composition of trace constituents (i.e. halogens) is a critical component due to all the interactions that can affect Hg oxidation.**
- **Sample preparation and cleaning of the test apparatus between tests takes on a greater emphasis.**

Mercury Testing Protocol

Here are the parameters identified (so far) that the Hg oxidation testing protocol needs to consider; plus the methodology to dose and measure each with sufficient accuracy:

- Temperature
- O_2
- SO_2
- H_2O
- NOx
- NH_3/NOx ratio
- Linear Velocity
- N_2
- Hg^0/Hg^{2+}
- CO
- HCl (halogen – fuel or additive)
- HBr (halogen – fuel or additive)
- HI (halogen – fuel or additive)
- SO_3
- CO_2
- Hydrocarbons

Duke Perspective: Catalyst Mercury Oxidation Testing

Purpose of lab testing

- Provide relative performance tracking on the ability of the catalyst to oxidize mercury at pre-established conditions.
- Currently no expectations for predicting actual SCR mercury oxidation in the field (too many variables).
- Keep the analysis costs “reasonable”.

Duke is leaning towards micro-scale reactors

- Micro-scale reduces cost of testing (construction of reactor and more importantly incremental testing costs).
- Micro-scale reduces the quantity of mercury that needs to be injected, measured, collected and properly discarded.

Path Forward

- Continue working with EPRI, STEAG and others to develop a cost effective test protocol.
- EPRI plans to issue Rev. 0 of the Mercury Oxidation Testing Guideline in March, 2015.
- Research and/or trial and error will likely be required in the short run as we begin working with a standardized guideline.
- In parallel with catalyst testing, continue to evaluate SCR overall performance in oxidizing mercury via field testing.
- This field performance can then be utilized to correlate the catalyst sample testing results and therefore its input into overall catalyst management planning.

Thanks Tom

Mercury balance in the power plant

Hg oxidation and reduction at SCR catalyst, ESP, FGD

Hg oxidation at conventional DeNOx catalyst: wide range

Hg reduction in FGD: Remission – release through stack

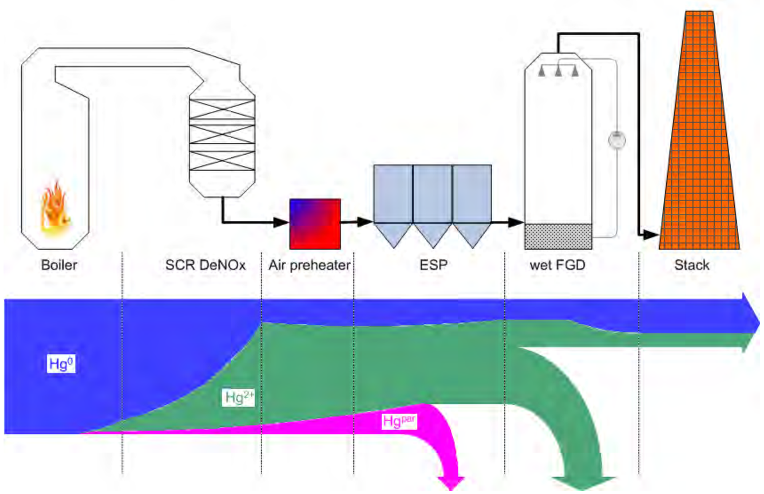


Fig. A: SCR catalyst with high efficiency in Hg oxidation

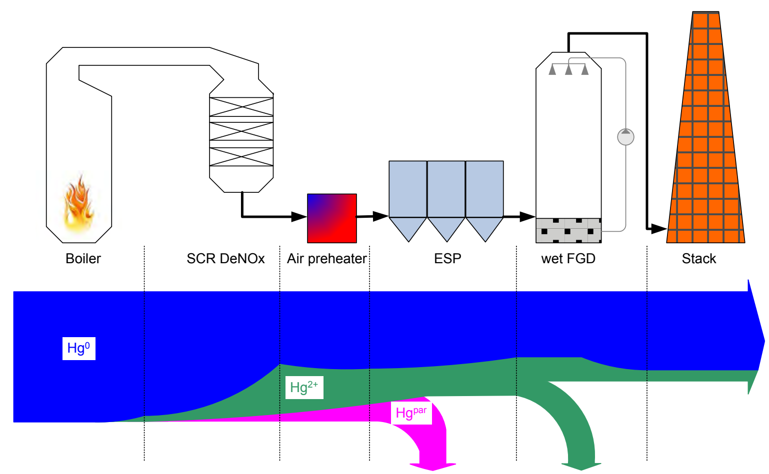


Fig. B: SCR catalyst with low efficiency in Hg oxidation

→→→Great importance of mercury oxidation at SCR catalyst

How can we control the mercury emissions?

- **We have Hg CEM monitors installed in the stack**
- **The FDG takes care of the Hg**
- **If NOT?**

- **We use additives to the coal or direct into the flue gas (i.e. chlorine, bromine, iodine) to support the reaction in the furnace and flue gas path**

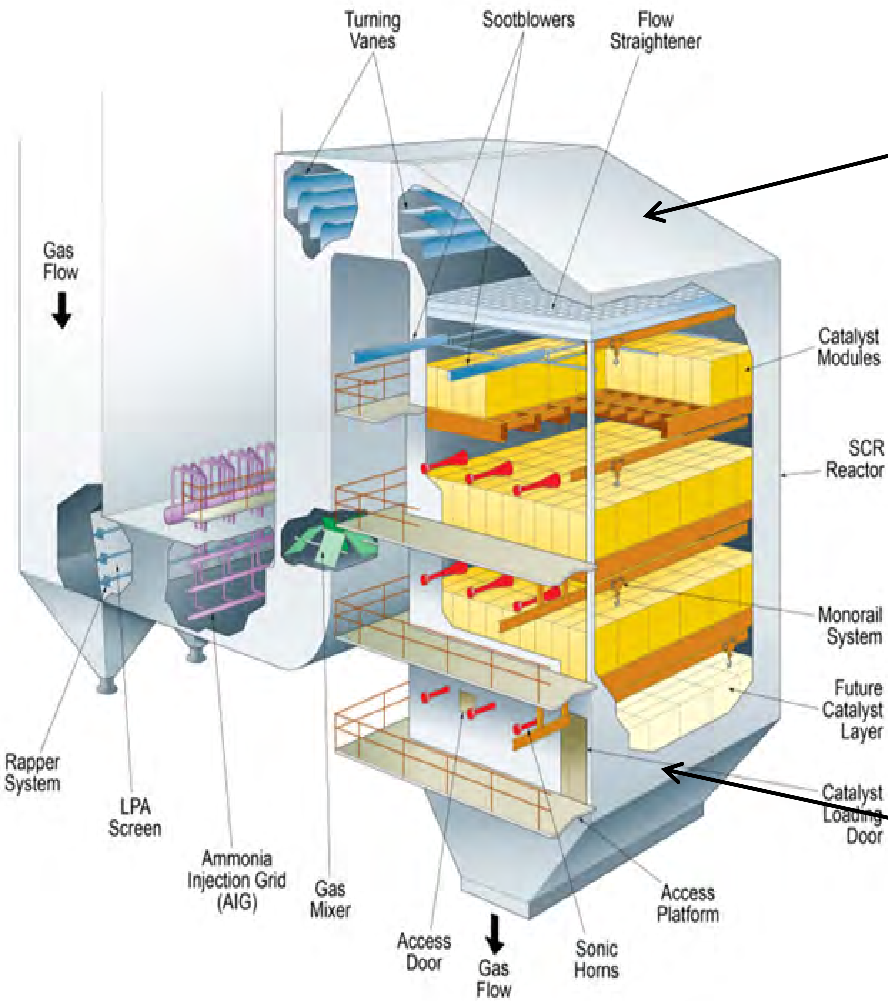
Economical issues?

- It does work!
- But it is not economical

- We want to use the SCR as the main boost

- And need to track the Hg oxidation in the SCR

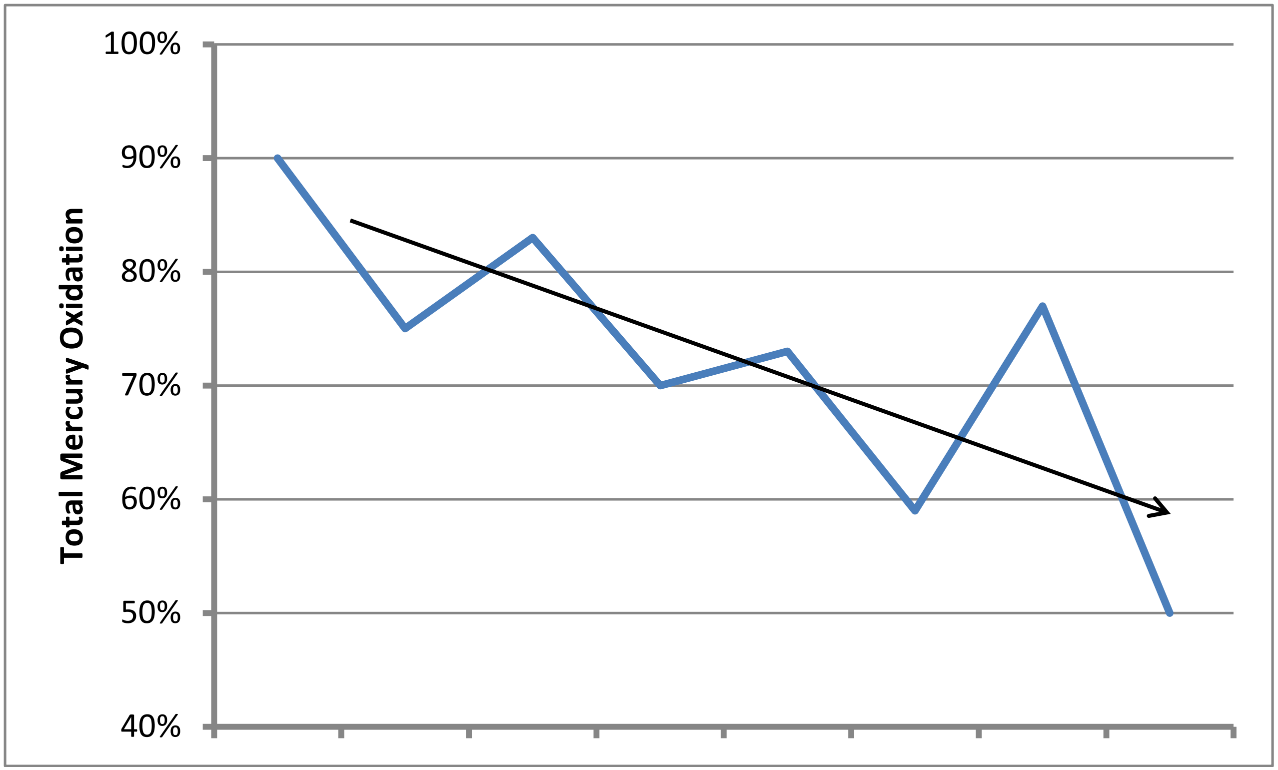
Field testing for mercury oxidation



Inlet
Hg_{el}, Hg^{2+}

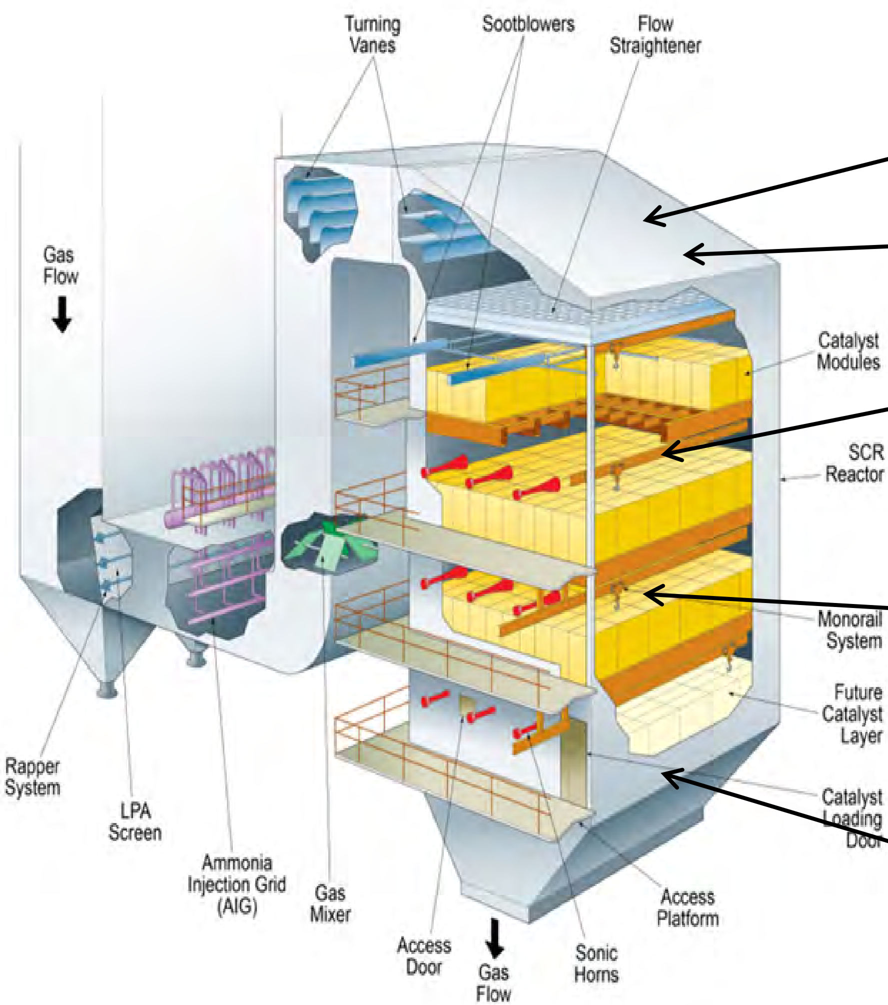
Outlet
Hg_{el}, Hg^{2+}

Mercury Oxidation Testing in the field



General Trend, but with much noise!

Field testing for performance tracking



Inlet
Hg_{el}, Hg^{2+}, NO, NH_3

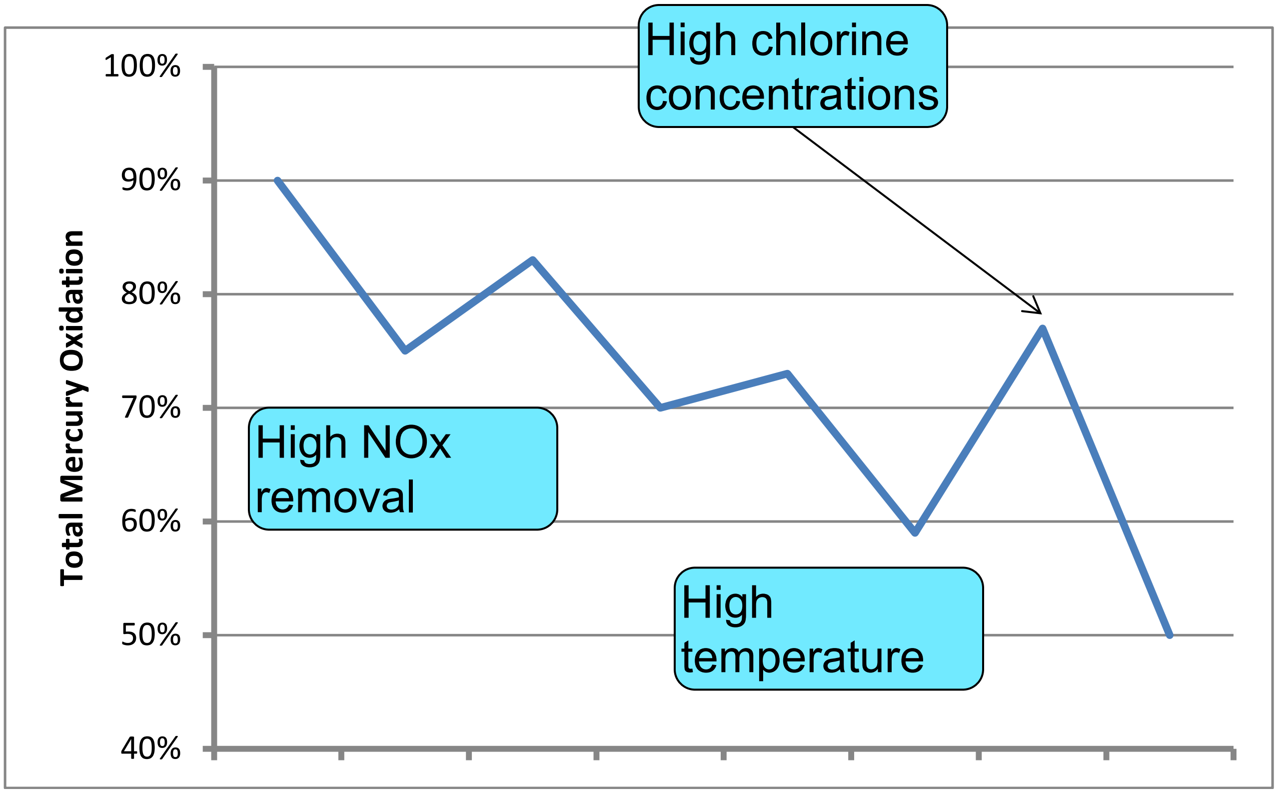
Temperature
Halogen
Unit load
Plugging
Mal distributions

After 1st layer
Hg_{el}, Hg^{2+}, NO, NH_3

After 2nd layer
Hg_{el}, Hg^{2+}, NO, NH_3

Outlet
Hg_{el}, Hg^{2+}, NO, NH_3

Mercury Oxidation Testing in the field - Causes



We still have a noisy curve, but we can explain it!

Can we use field testing for our managing program?

- Field Testing is not practical
- Different operating parameters cause noisy trend
- Resulting in wrong interpretations due to unknown and uncontrolled parameter

- We need to move the testing into a controlled environment

- But we need field testing to correlate lab results

Mercury lab testing

- **For a precise and repeatable results, the performance testing needs to be done in the lab**
- **Utilities decided early to add Hg testing in the existing NOx EPRI protocol**
- **Duke and STEAG were along the committee to develop a practical guideline**

How to develop a good testing guideline

- **The first Hg protocol ask for a very complicated setup**

Parameter	Target Value for Field Prediction and releative Testing	Allowable Deviation from Target	Allowable Drift
Temperature	Field Value	± 10 °F absolute	± 5 °F absolute
AV	Field Value	± 3 % relative	± 2 % relative
O_2	Field Value	± 0.2 % absolute	± 0.1 % absolute
H_2O	Field Value	± 2 % absolute	± 1 % absolute
CO_2	Field Value	± 2 % absolute	± 1 % absolute
NO_x	Field Value	± 2 % relative	± 1 % relative
α (NH_3/NO_x ratio)	Field Value	± 0.05 % absolute	± 0.02 % absolute
SO_2	Field Value	± 10 % relative	± 5 % relative
SO_3	Not Required / Field	± 2 ppm absolute	± 1 ppm absolute
HCl	Field Value	± 1 ppmv absolute (5 - 20 ppmv) ± 2 ppmv absolute (> 20 - 40 ppmv) ± 5 ppmv absolute (> 40 ppmv)	± 0.5 ppmv absolute (5 - 20 ppmv) ± 1 ppmv absolute (> 20 - 40 ppmv) ± 3 ppmv absolute (> 40 ppmv)
HBr	Not Required / Field Injection Level	± 0.02 ppmv absolute (0.5 - 1 ppmv) ± 0.05 ppmv absolute (> 1 - 5 ppmv) ± 0.3 ppmv absolute (> 5 - 10 ppmv)	± 0.01 ppmv absolute (0.5 - 1 ppmv) ± 0.03 ppmv absolute (> 1 - 5 ppmv) ± 0.2 ppmv absolute (> 5 - 10 ppmv)
CO	Field Value	± 2 % relative	± 1 % relative
Hg^0	Field Value	± 5 μg/Nm³ absolute	± 2 μg/Nm³ absolute
N_2	Balance	NA	NA

Epri guideline
– a dead end

The Intention was good

- We added all the known and partial known factors
- We tightened nearly all the loop holes

- But it was unpractically and too expensive

Epri guide line
– a new beginning

So we stepped back

We kept the guideline simple and practical

- **Use a set of standard conditions or adjust as needed**
- **Micro, semi and full bench as an option**
- **Stick to the known factors**

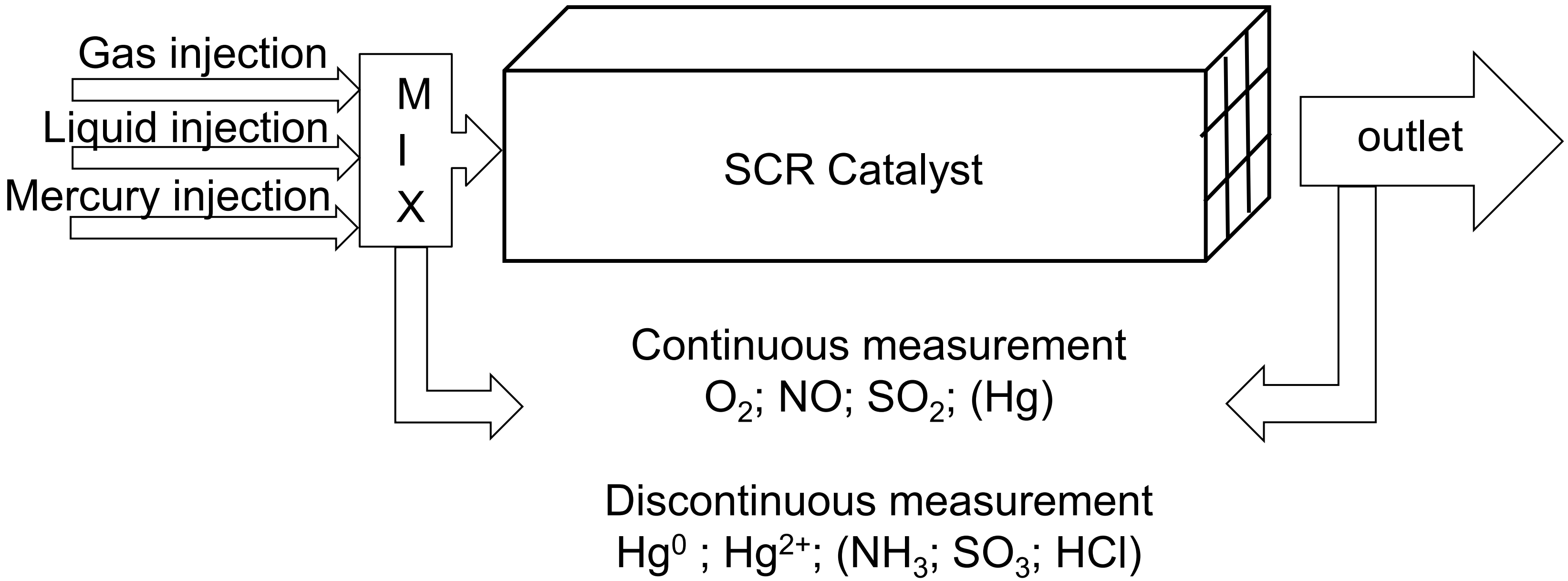
But the utility can agree with the lab for special conditions if required!

Current EPRI Protocol

Current EPRI Protocol (in progress)

Parameter	Target Value	Allowable Deviation from Target	Allowable Drift
Temperature	700 °F or Determined by Lab and End User	± 10 °F	± 5 °F
AV	18.0 m/hr (STP), or Determined by Lab and End User	± 0.5 m/hr	± 0.3 m/hr
O_2	3.0 % (dry)	± 0.5 %, absolute	± 0.3 %, absolute
H_2O	8.0 %	± 2 %, absolute	± 1 %, absolute
CO_2	0 % or as generated	--	--
NO_x	0 ppmvd, or Determined by Lab and End User	± 10 % of value	± 5 % of value
α (NH_3/NO_x)	0.0, or Determined by Lab and End User	± 10 % of value	± 5 % of value
SO_2	1000 ppmvd, or Determined by Lab and End User	± 10 % of value	± 5 % of value
SO_3	not required	--	--
HCl	75 ppmvd, or Determined by Lab and End User	± 10 % of value	± 5 % of value
HBr	not required	--	--
CO	0 ppmvd, or Determined by Lab and End User	± 10 % of value	± 5 % of value
Hg^0	50 - 100 µg/m³ (STD, dry)	± 10 % of value	± 5 % of value
Hg^{2+}	less than 7 % of total mercury	--	--
N_2	Balance	NA	NA

How to test mercury oxidation in the lab

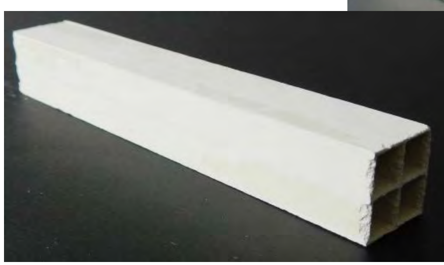


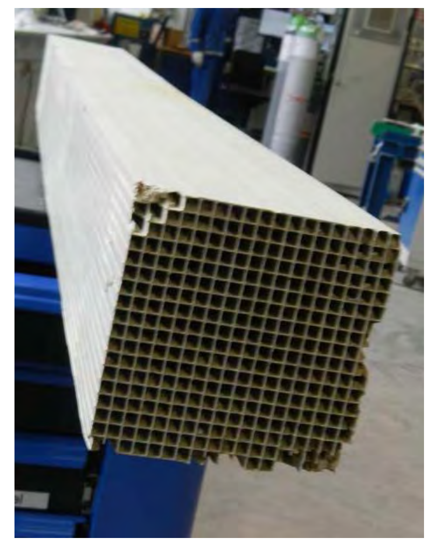
- Temperature controlled environment (400 to 840 °F)
- Digital multi component gas and liquid mixing system → close to plant parameters
- Measurement up and down stream of catalyst
- NOx removal and SO_2/SO_3 conversion rate testing optional

Steag micro reactor

Micro, Semi and bench Testing

Micro reactor	Semi Scale	Bench Scale
2x2 Cells	5x5 Cells	20x20 Cells
100mm long	200 – 500mm long	Full size – 1350mm



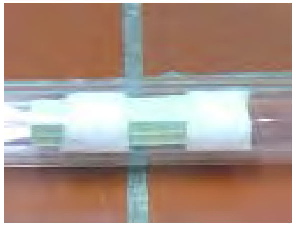


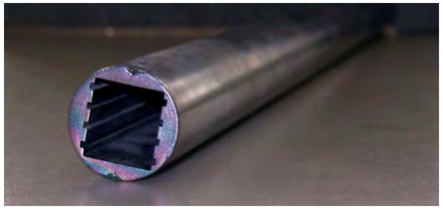
Sample preparations

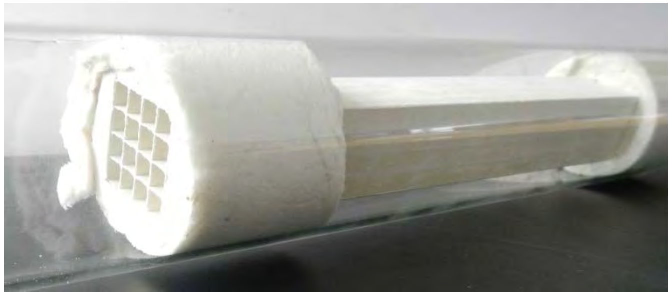
Catalyst preparation for micro tests:

– cutting the catalyst (honeycomb: band saw
plate type: mechanical shears)

– placing the catalyst (honeycomb: fixed with glass wool
plate type: fixed in special fixture)







Hg sampeling

continuous

Different apparatus

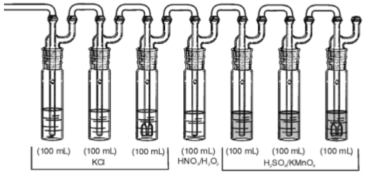
- wet chemical methods
- with converters
- using gold traps

+ records peaks directly
+ shows trending

- often inapplicable for low concentrations
- often cross sensitivity to other gas components

discontinuous

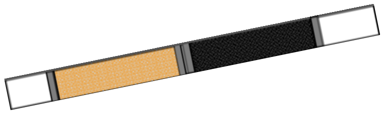
Ontario Hydro ASTM D 6784-02



+ used and tested since 1994

- difficult to handle

sorbent trap method



+ easier to use

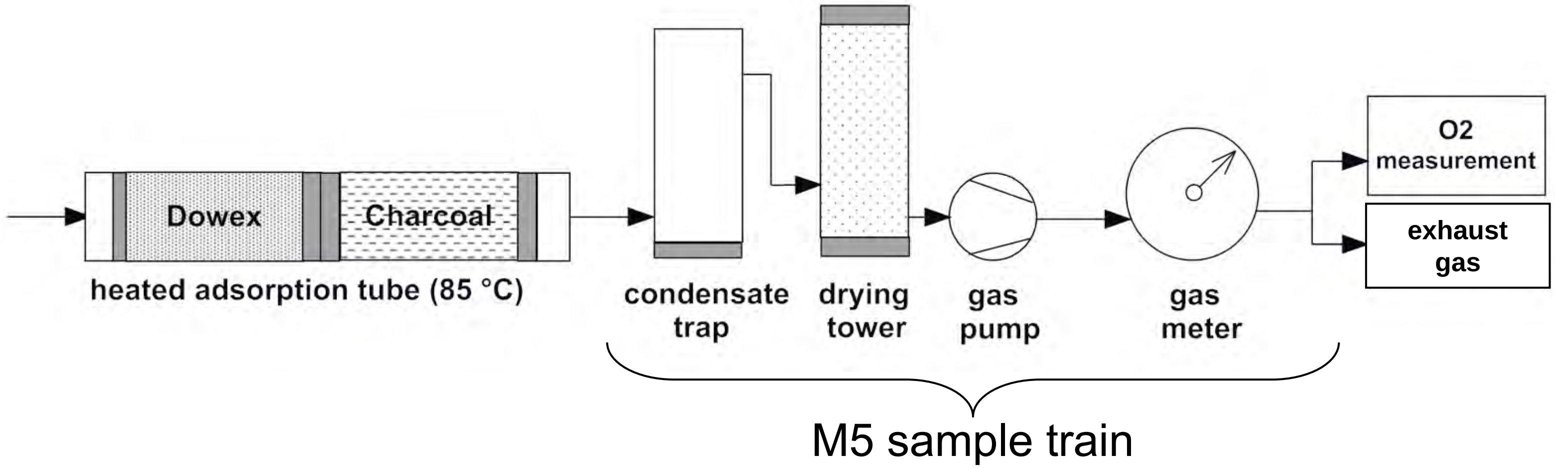
- Different traps available
  you need to pick the right one for the application

Dowex – sorbent traps

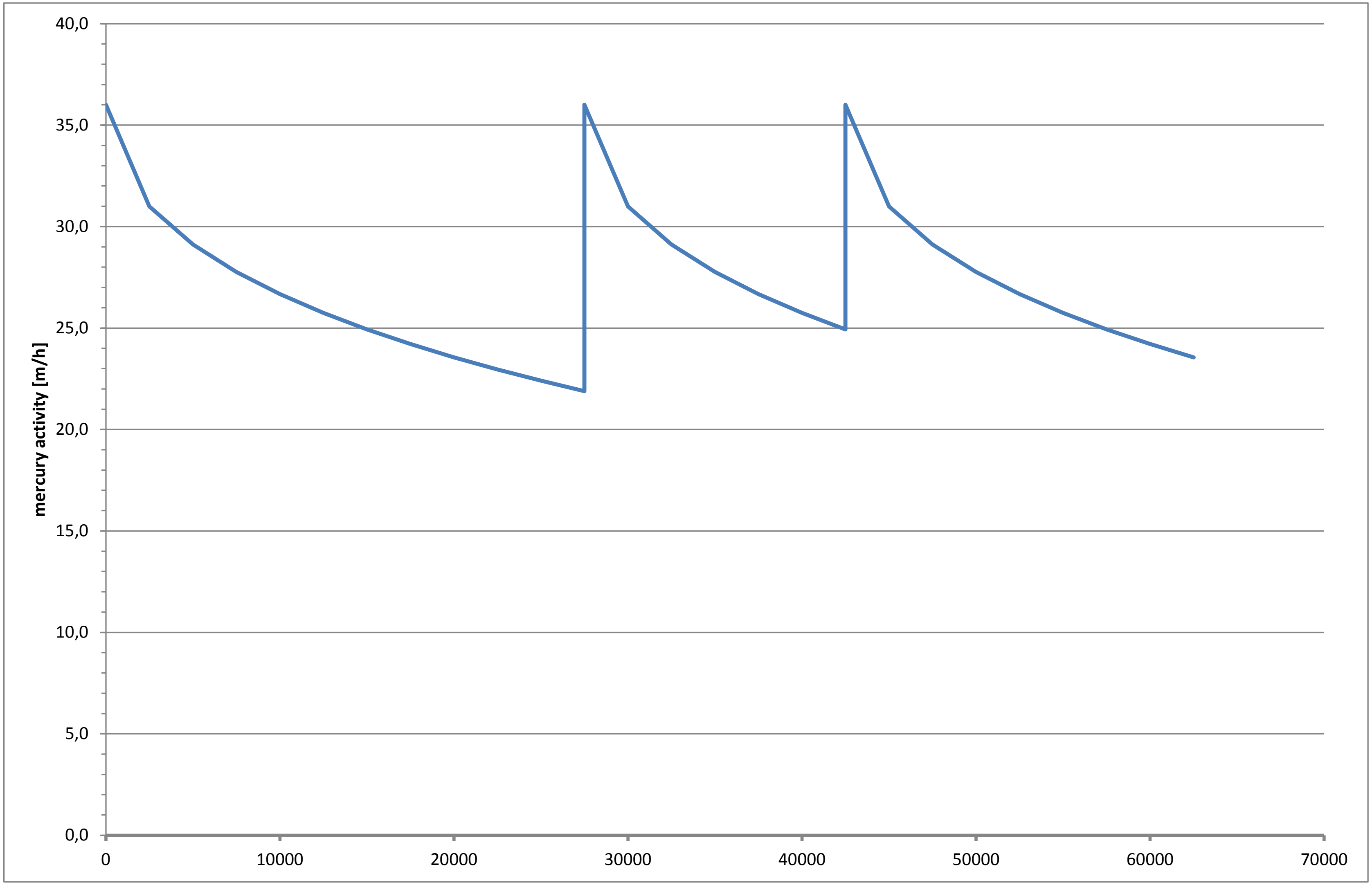
Dowex – activated carbon trap method

- gas sampling by pulling gas through adsorber tube (45 min)
- three sample trains: one at inlet and two at outlet of catalyst
- three sequential samplings per location and catalyst (3 x 45 min)

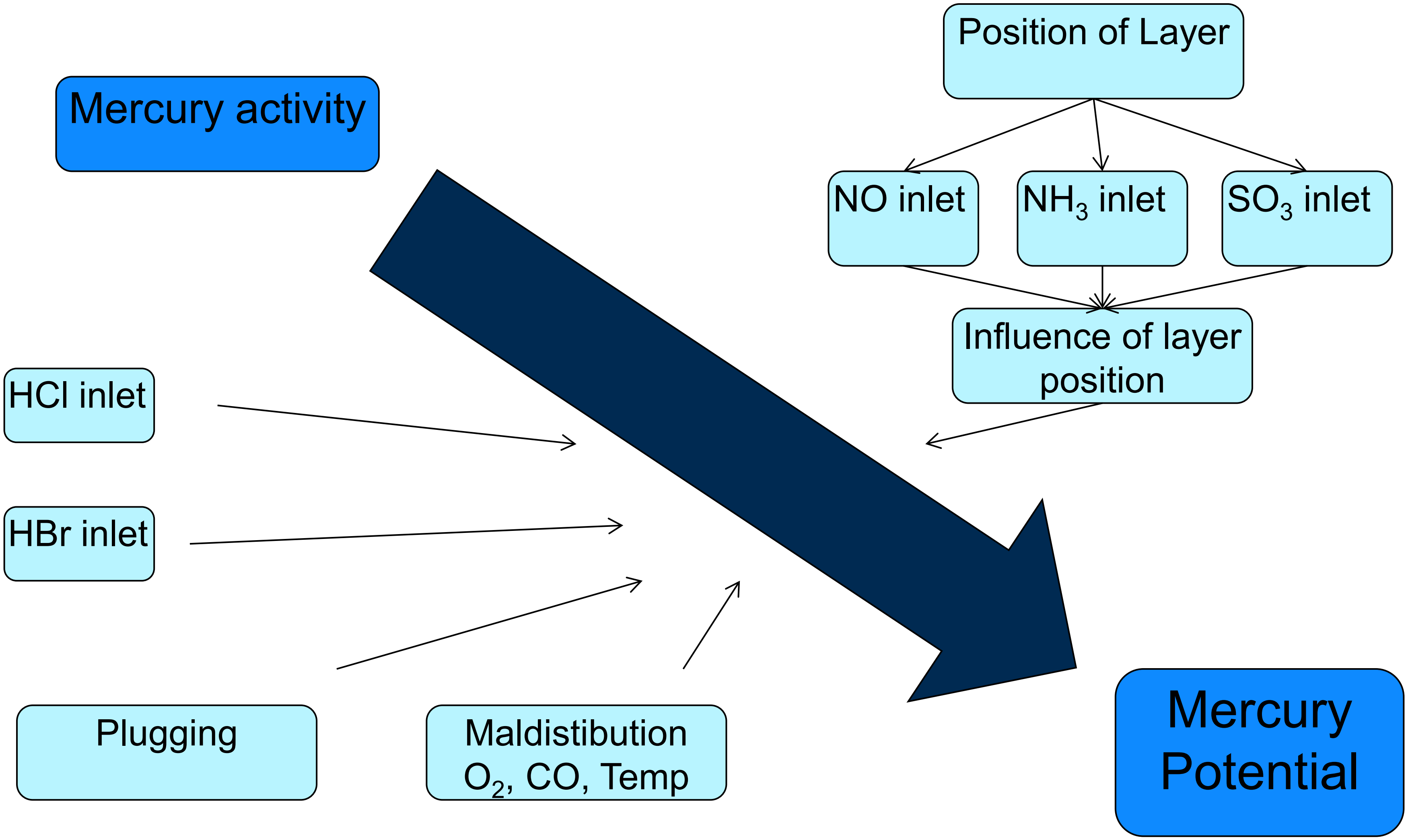
→ **nine samples of Dowex (Hg^{2+}) and charcoal (Hg^0) to analyze on each test run (1 day)**



Mercury activity trend



From Mercury activity to potential



Best Way to Do?

close to Layer

Test under the layer condition

+ easy transition from K to P possible

- Must test all layer first for NOx
- Long and expensive Test setup
- Can not test only one Layer

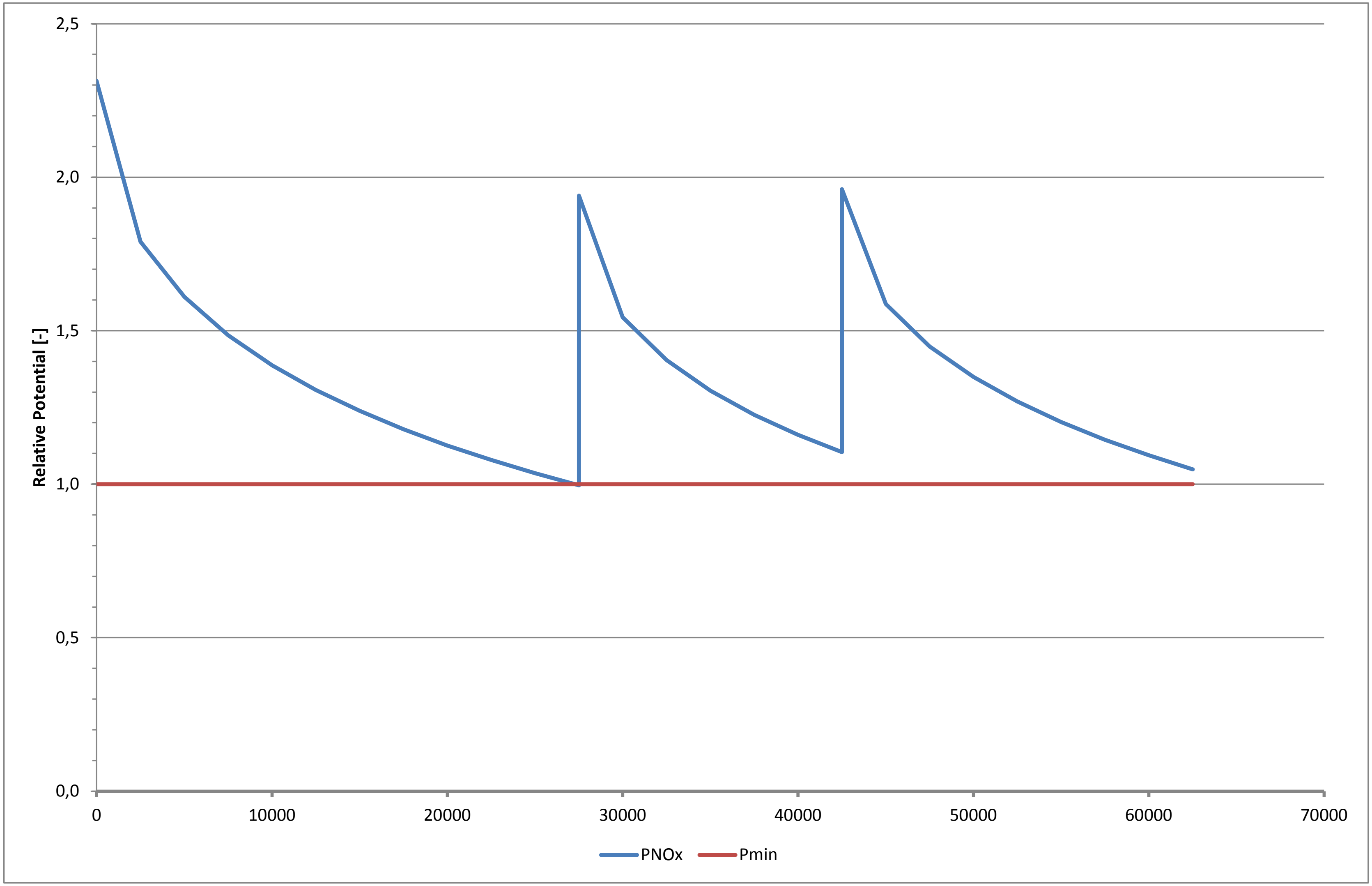
standard set

Testing all layers same

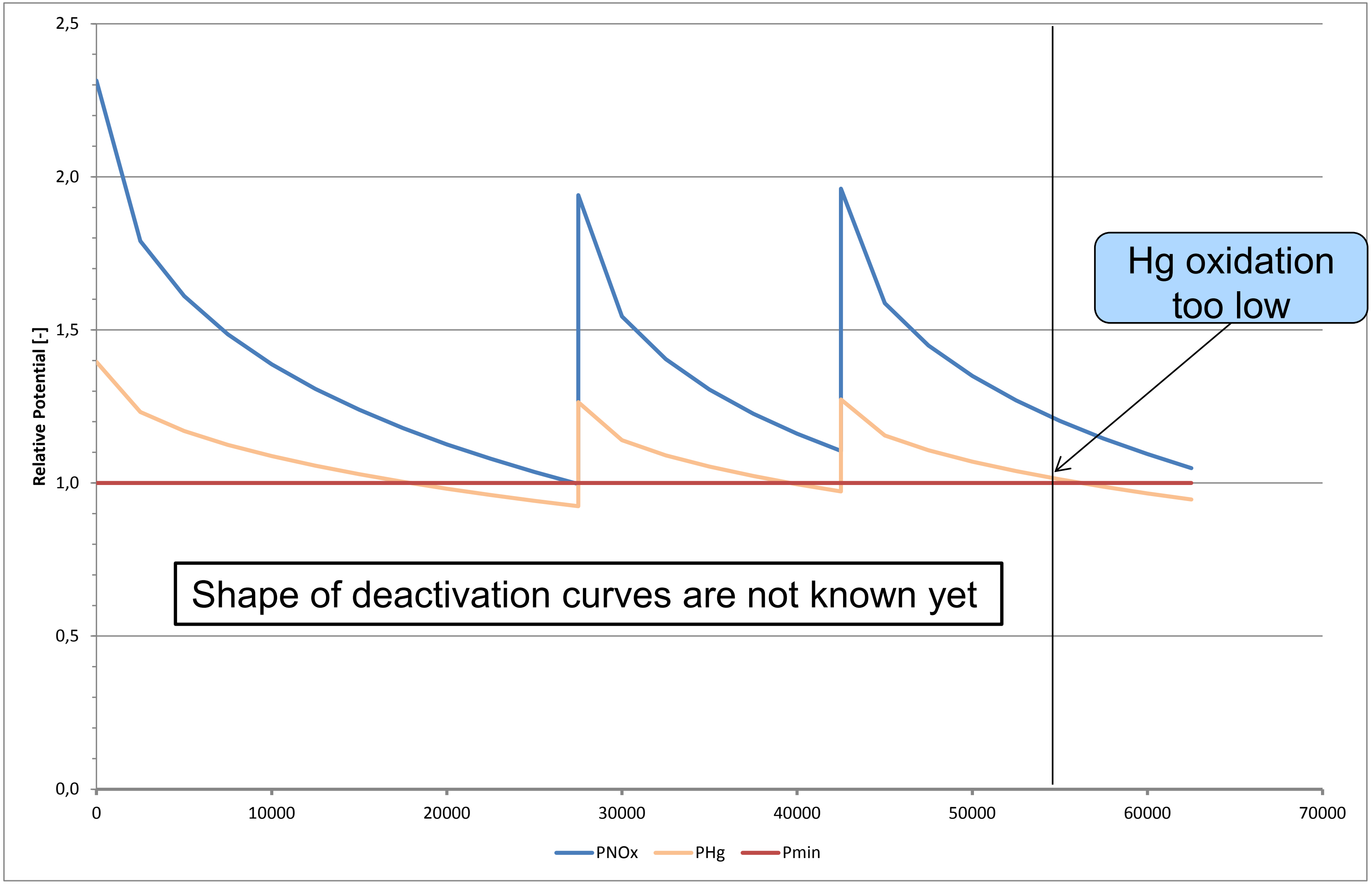
+ simple test setup
+ shows trending from activity lost only

- Model needed to apply the layer factor

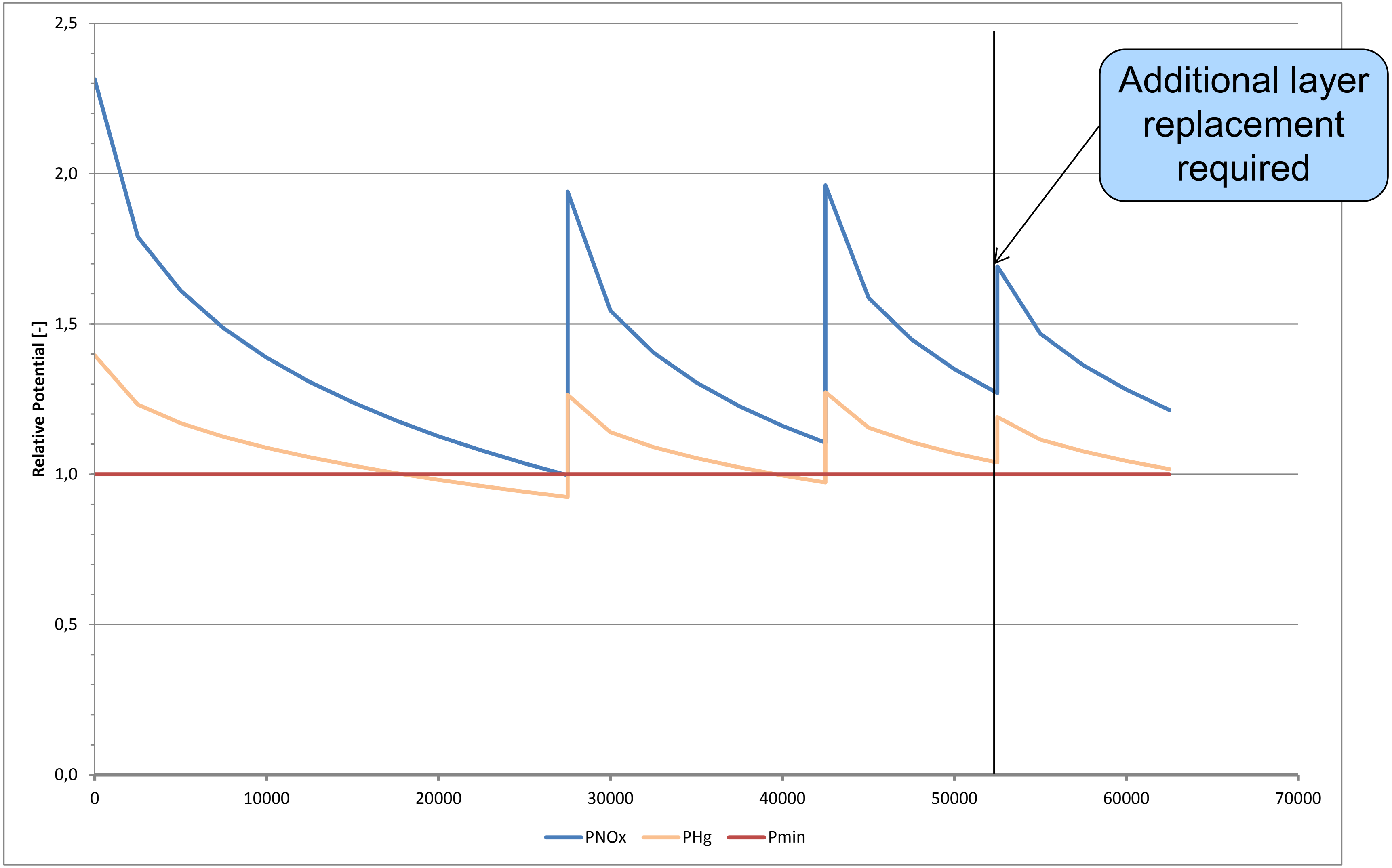
Catalyst management -current state



Trend of NOx and mercury performance



Catalyst Management including NOx and mercury



Summary

- The SCR support the FDG in removing the mercury from the flue gas
- A specialized catalyst managing program saves money in additional additives
- Field testing only provides a single data point and can not be used for tracking the catalyst performance
- Duke and Steag are working together with the EPRI in finishing a guideline for mercury lab testing
- The current program allows us to track the mercury oxidation
- Further research is required to implement a full NOx and mercury catalyst managing program

steag