REINHOLD ENVIRONMENTAL Ltd.

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Mercury Oxidation Improvements via Catalyst and Coal Additives

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- **Mercury behavior can be inconsistent and counterintuitive.**

- **Plots and other information given are examples for general understanding purposes and don’t necessarily apply to any particular situation.**

- **Be careful in assuming that theoretical behavior will apply, or in extrapolating behavior at one unit to another.**

Mercury Oxidation - Fundamentals

Mercury "oxidation" refers to the combining of elemental mercury with other chemical species through the oxidation process. For coal-fired boilers, those oxidizing species are halogens, primarily Chlorine and Bromine.

Mercury Oxidation "rate" is the proportion of elemental mercury entering the system that is oxidized.

$$\text{Hg Oxid. Rate} = (Hg^0_{in} - Hg^0_{out})/Hg^0_{in}$$

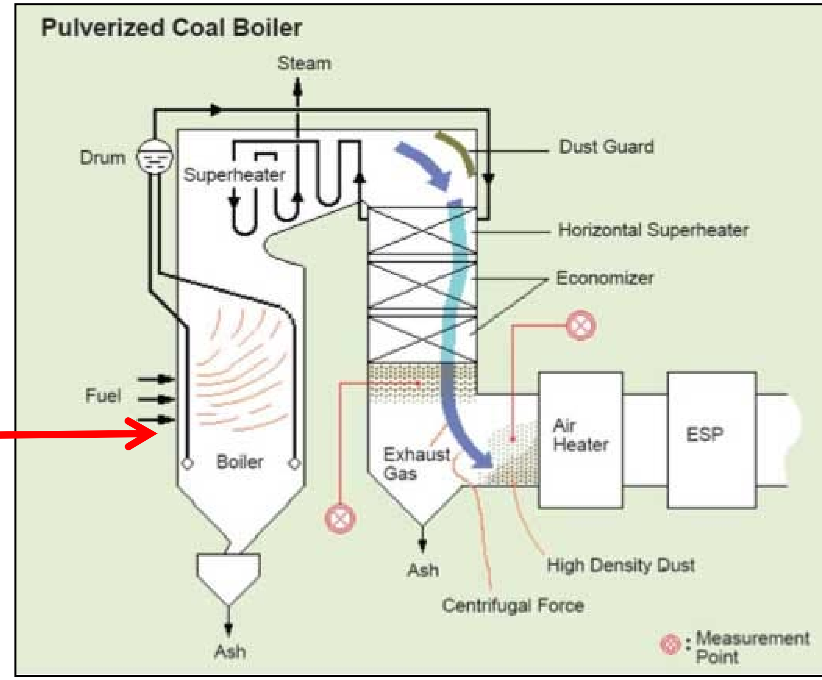
Mercury Oxidation "potential" is a handy parameter similar to deNOx potential for reactor design work.. Highly specific to AV and operating conditions

$$\text{Hg Oxid. Potential} = -AV*\ln(1-\text{rate})$$

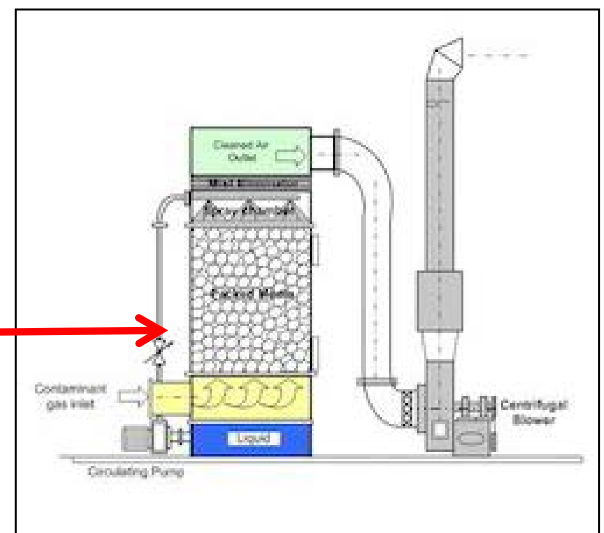
Additives

Purpose of <u>boiler</u> additives is to increase halogens to improve mercury oxidation across the SCR, and potentially downstream equipment.

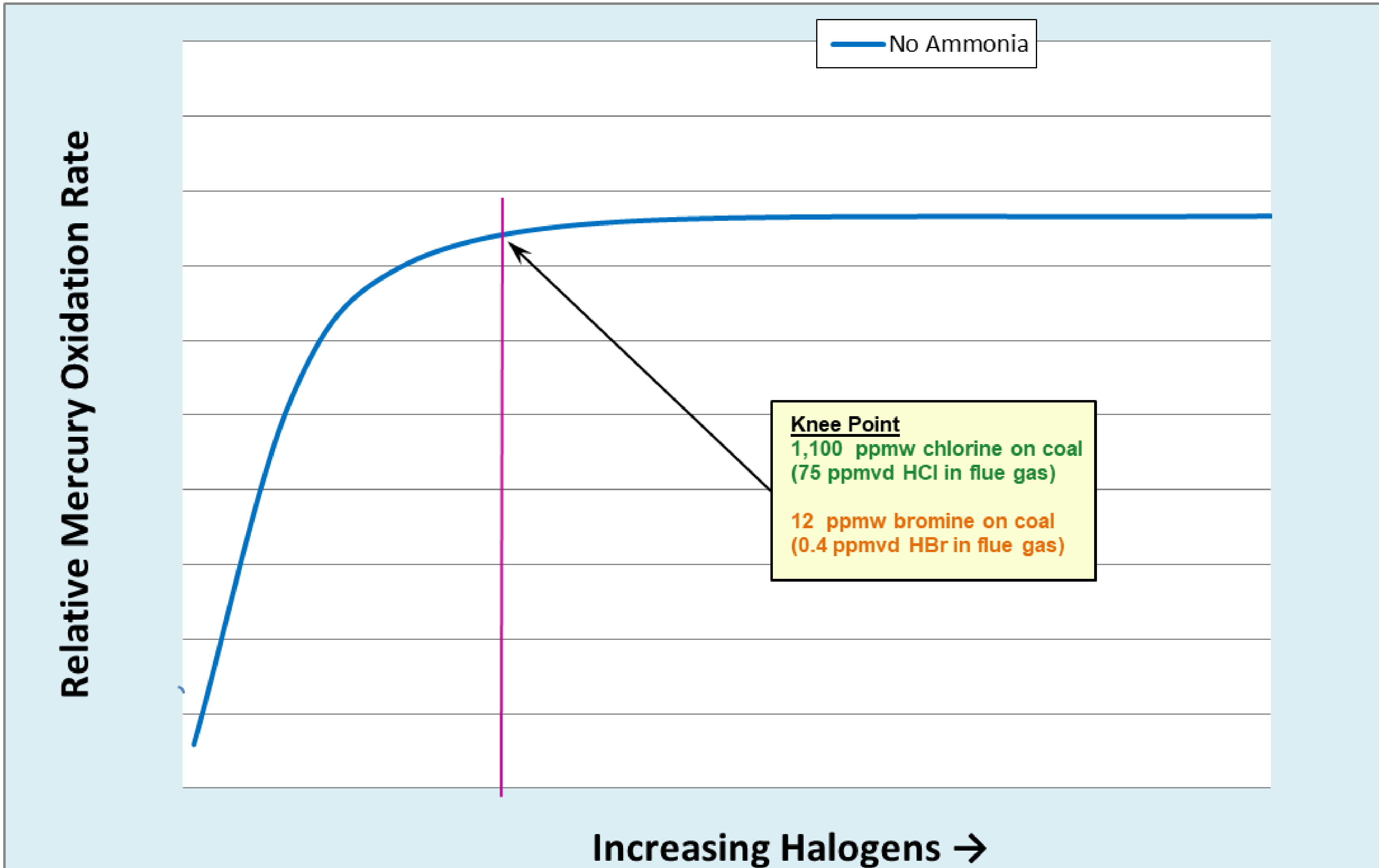
Although not considered an "additive" coal blending or switching can have a similar effect, at least to chlorine supplementation.



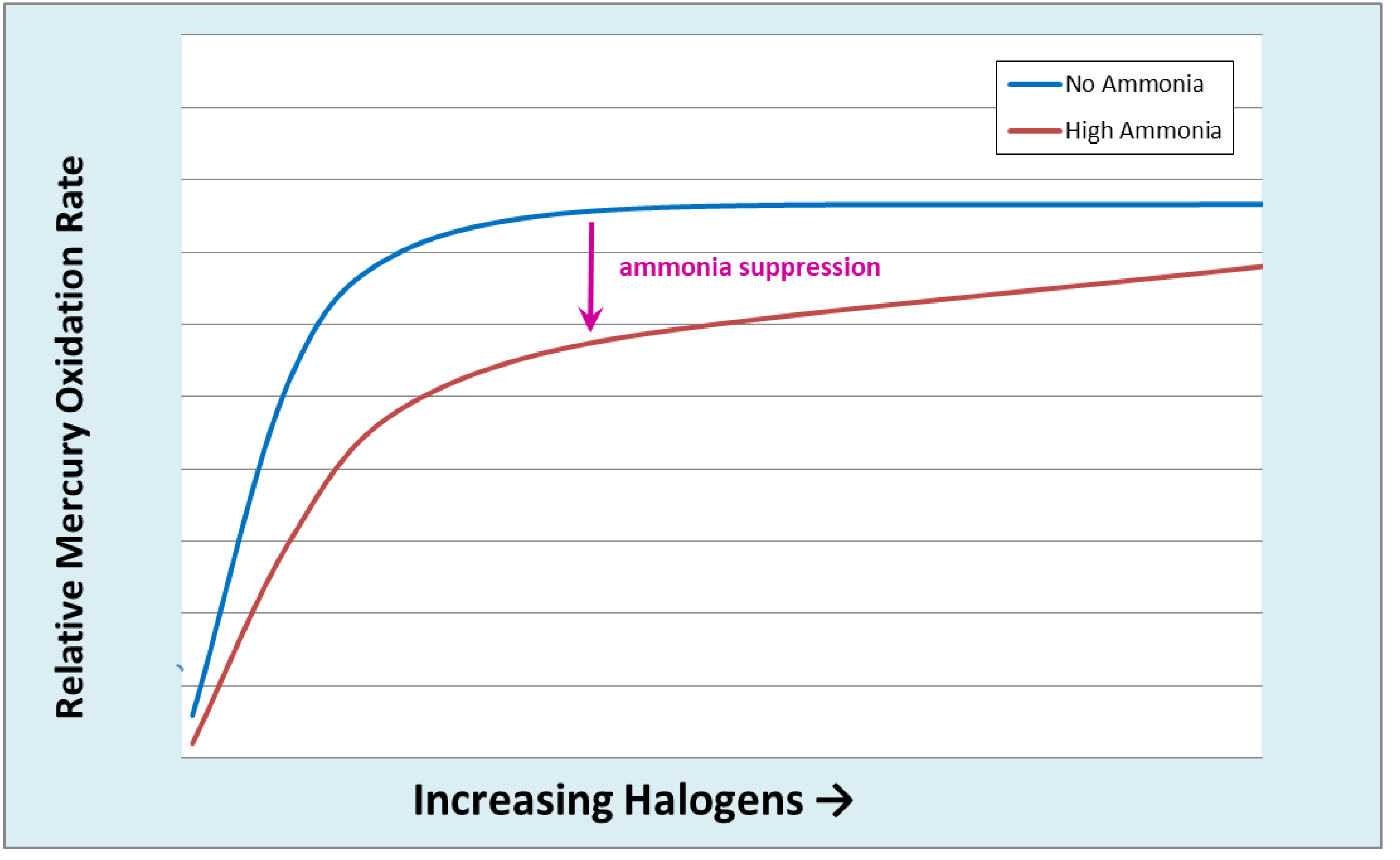
Scrubber additives may also be used to help capture mercury in the scrubber, and especially to limit re-emissions. These additives are not discussed.



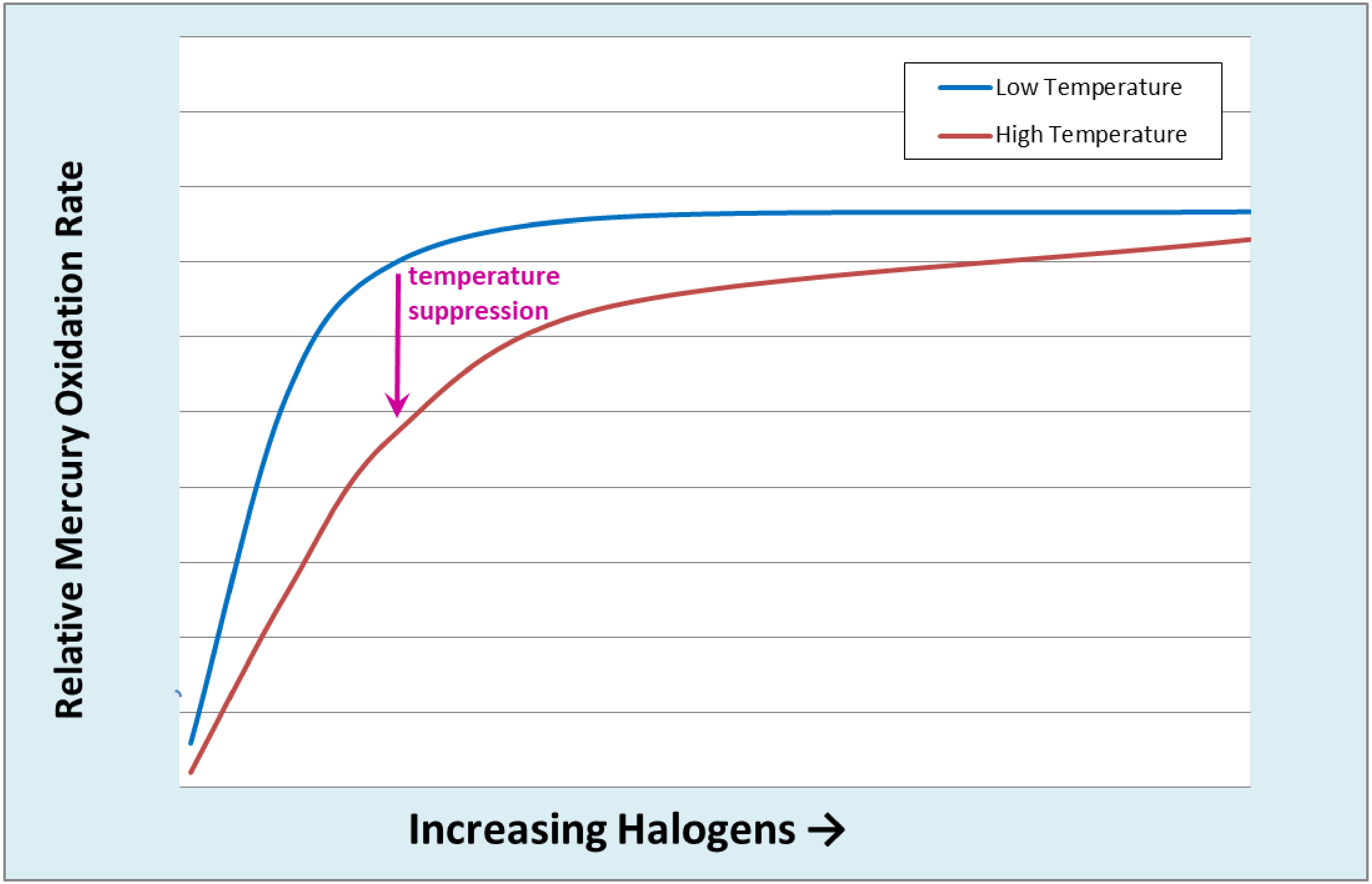
General Effect of Halogens



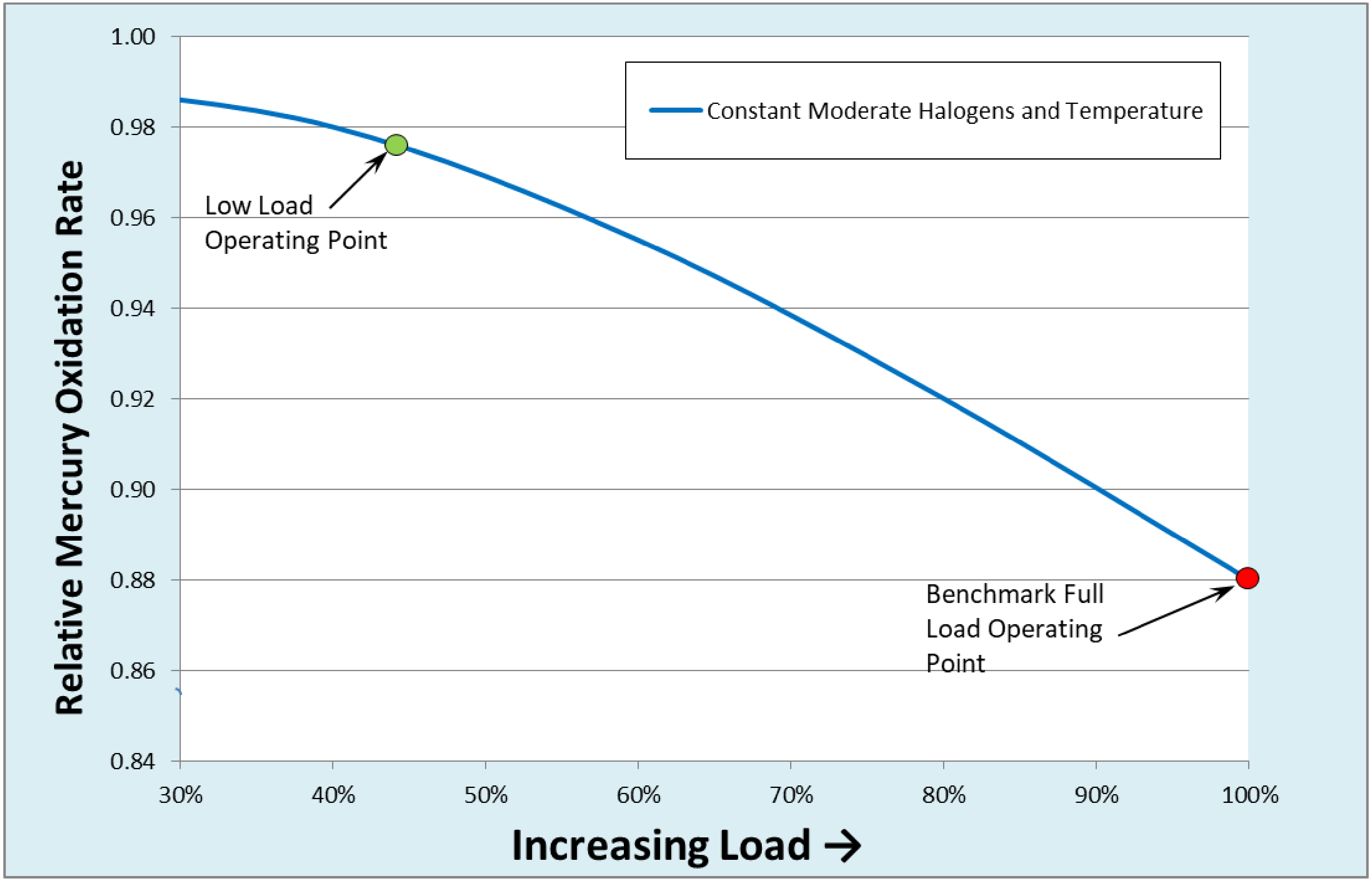
Effect of Ammonia on SCR



Effect of Temperature on SCR



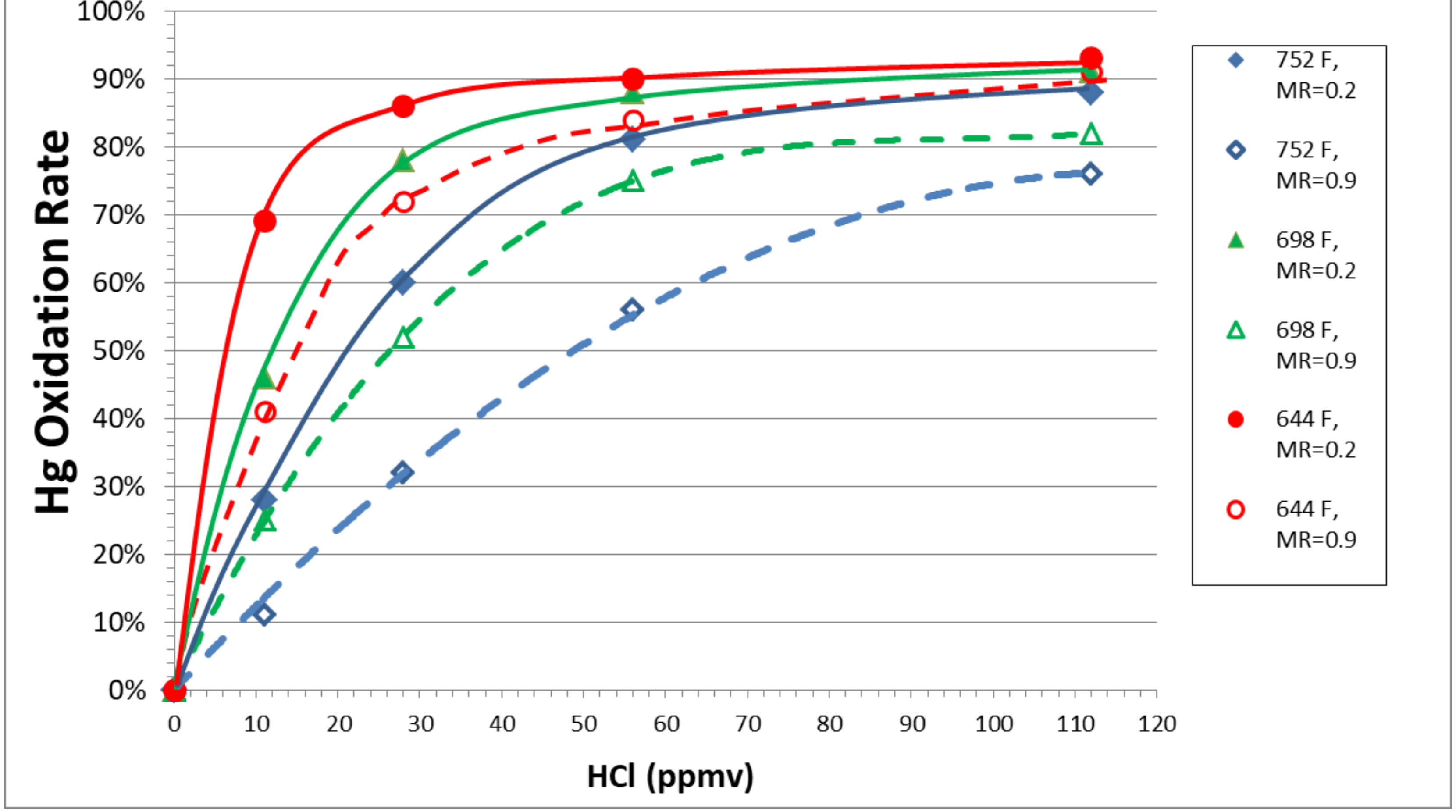
Effect of Flow Rate on SCR (Load)



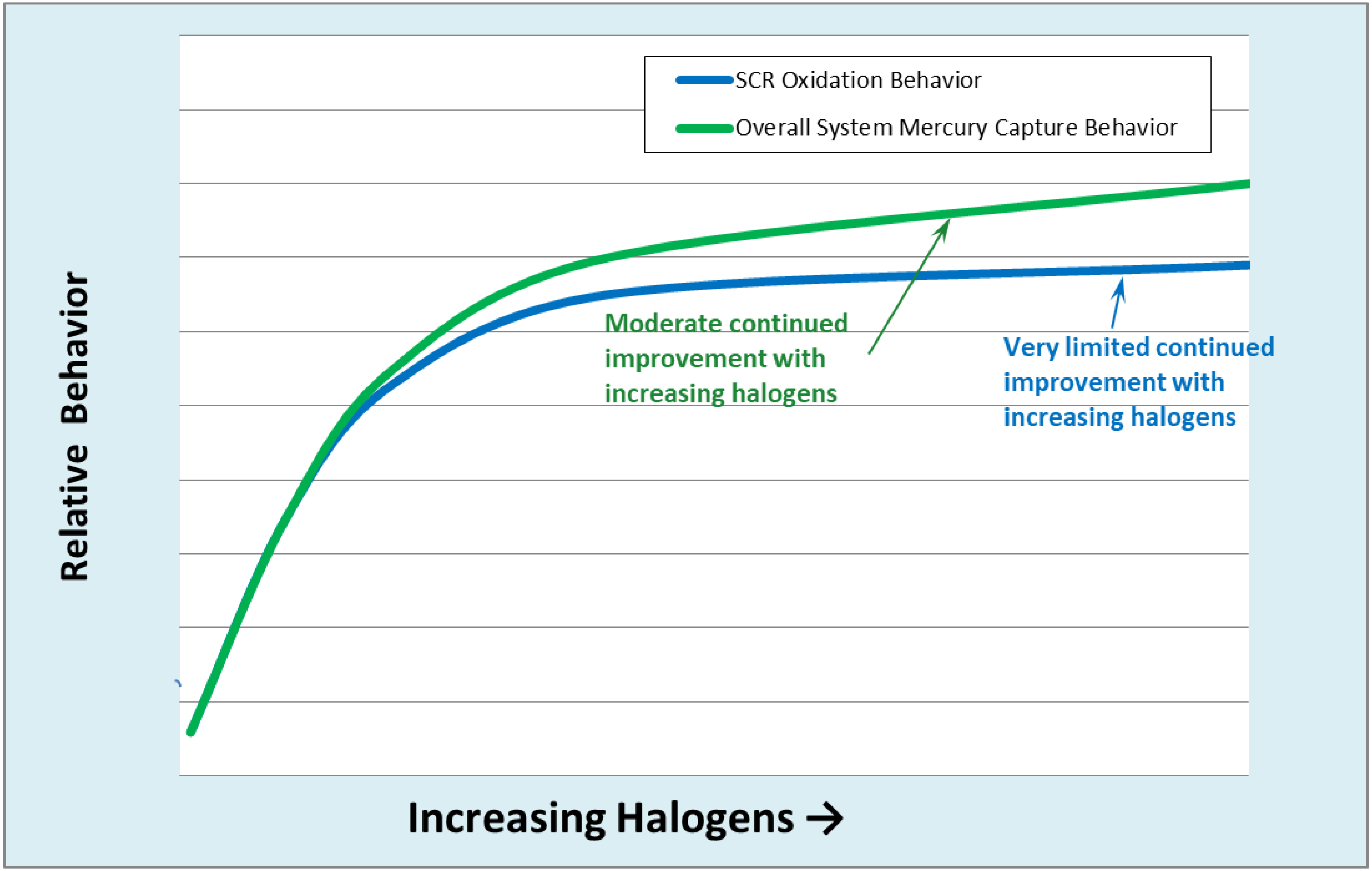
SCR Effects are Inter-related!

- Halogens
- Temperature
- Ammonia
- Flow Rate
- O_2
- SO_2
- H_2O

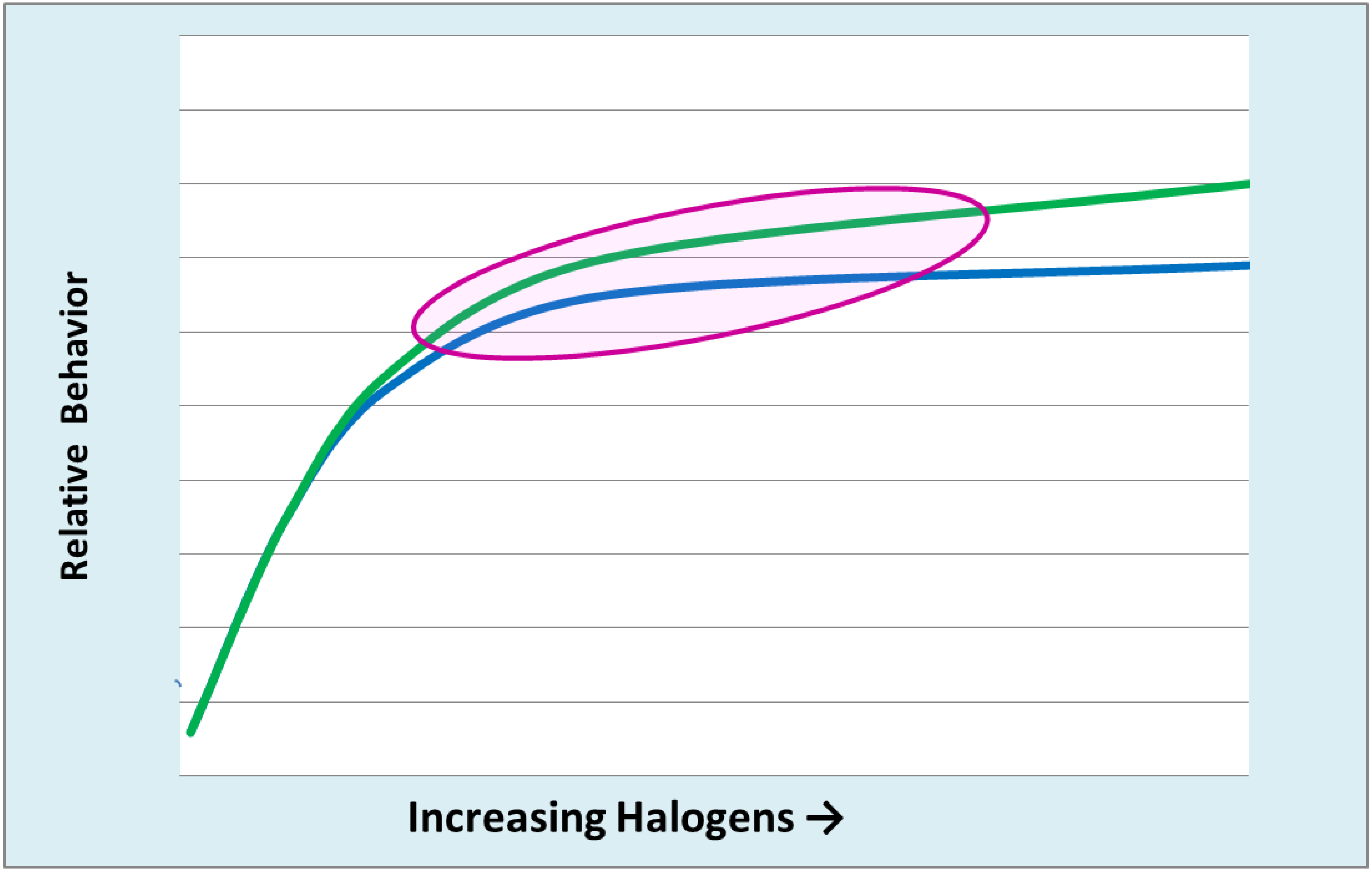
Example of Inter-relationship of HCl, Temperature, and Ammonia



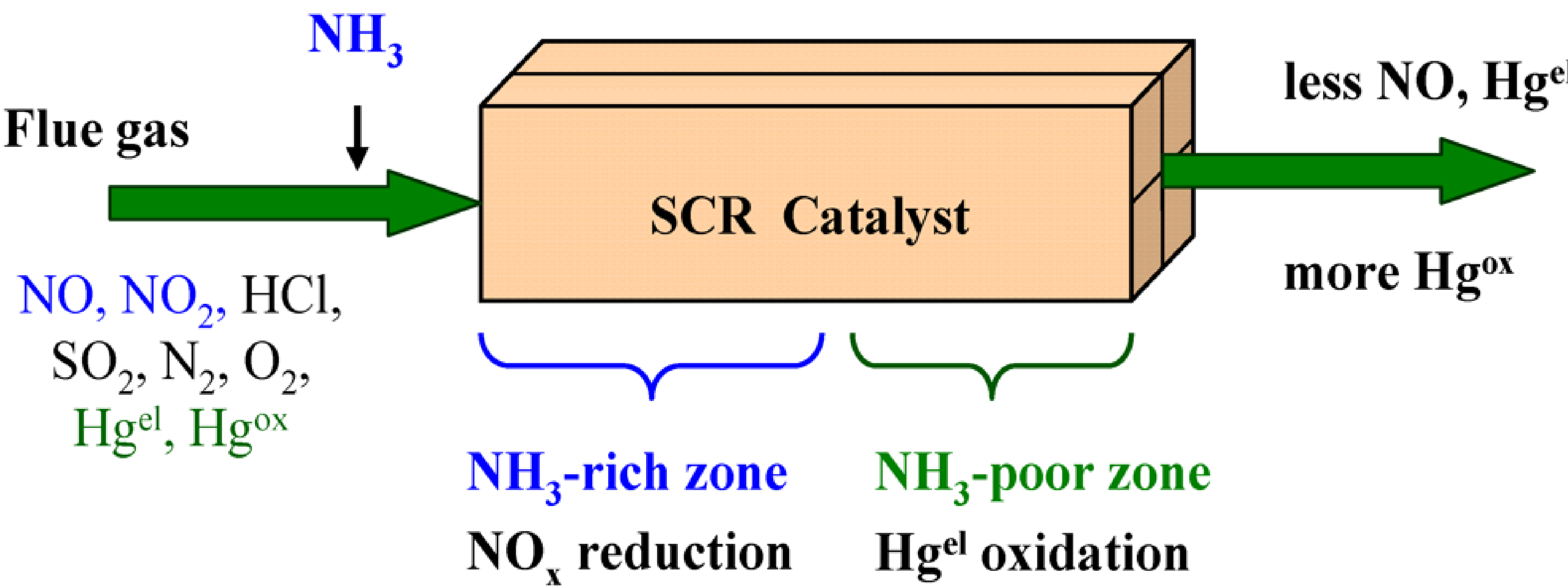
General Behavior of SCR vs. System Capture



Where's the "Sweet Spot" ?



Catalysts



NH_3
Flue gas
SCR Catalyst
less NO, Hg^{el}
more Hg^{ox}
NO, NO_2, HCl,
SO_2, N_2, O_2,
Hg^{el}, Hg^{ox}
NH_3-rich zone
NO_x reduction
NH_3-poor zone
Hg^{el} oxidation

Catalysts Facilitate Chemical Reactions

3 Primary Reactions of Concern

Reactions are Inter-related

1. DeNOx Reaction

$NOx + NH_3 \rightarrow N_2 + H_2O$

2. SO_2 Oxidation/Conversion

$SO_2 + O_2 \rightarrow SO_3$

3. Mercury Oxidation

$Hg + Halogen \rightarrow HgCl_2$ or $BgBr_2$

Catalyst Specific Behavior Factors to Consider

Design of Catalyst (intrinsic mercury oxidation)

- DeNOx activity
- SO_2 conversion
- Advanced vs. conventional

Amount of Catalyst

- Volume
- Pitch (specific surface area)

Catalyst Management

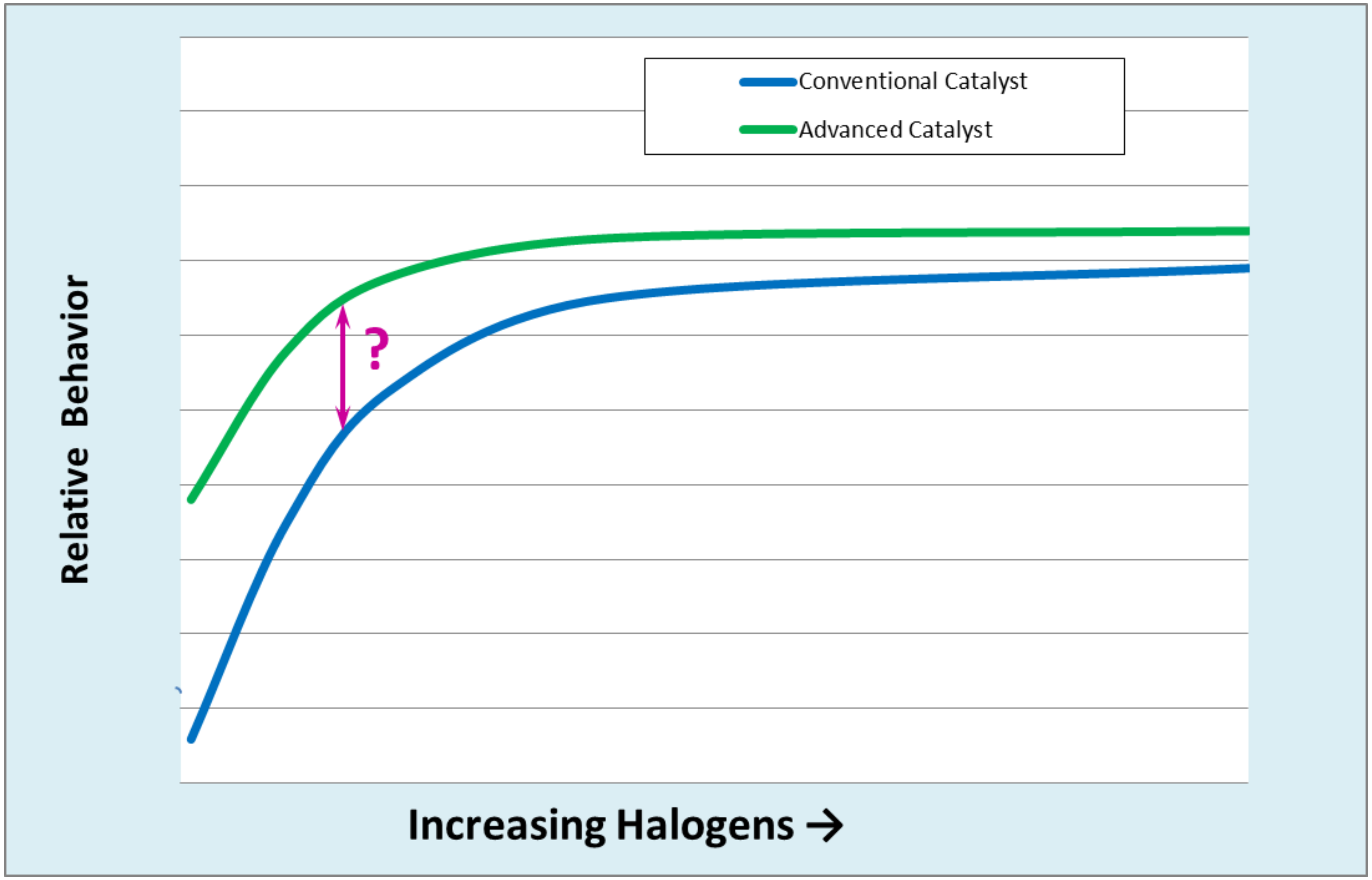
- Mercury oxidation potential will follow sawtooth pattern similar to deNOx potential

Catalyst Aging (deactivation)

- Loss of mercury oxidation activity similar to loss of deNOx activity

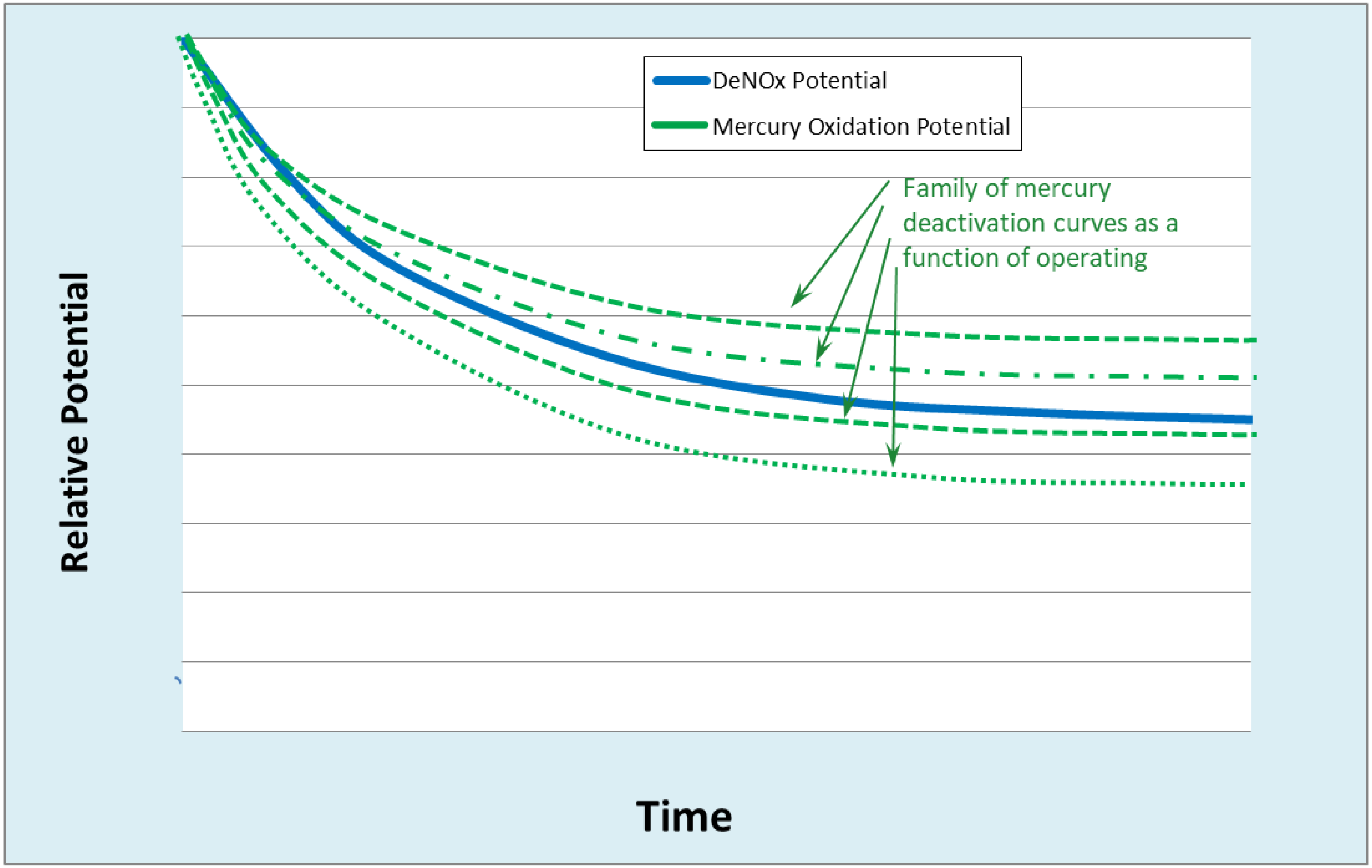
Advanced Catalysts

- **How much Hg oxidation "differential" do we get and under what conditions?**
- **What are the tradeoffs (lowered deNOx activity, higher SO_2 conversion, etc.)?**
- **What is the cost differential?**



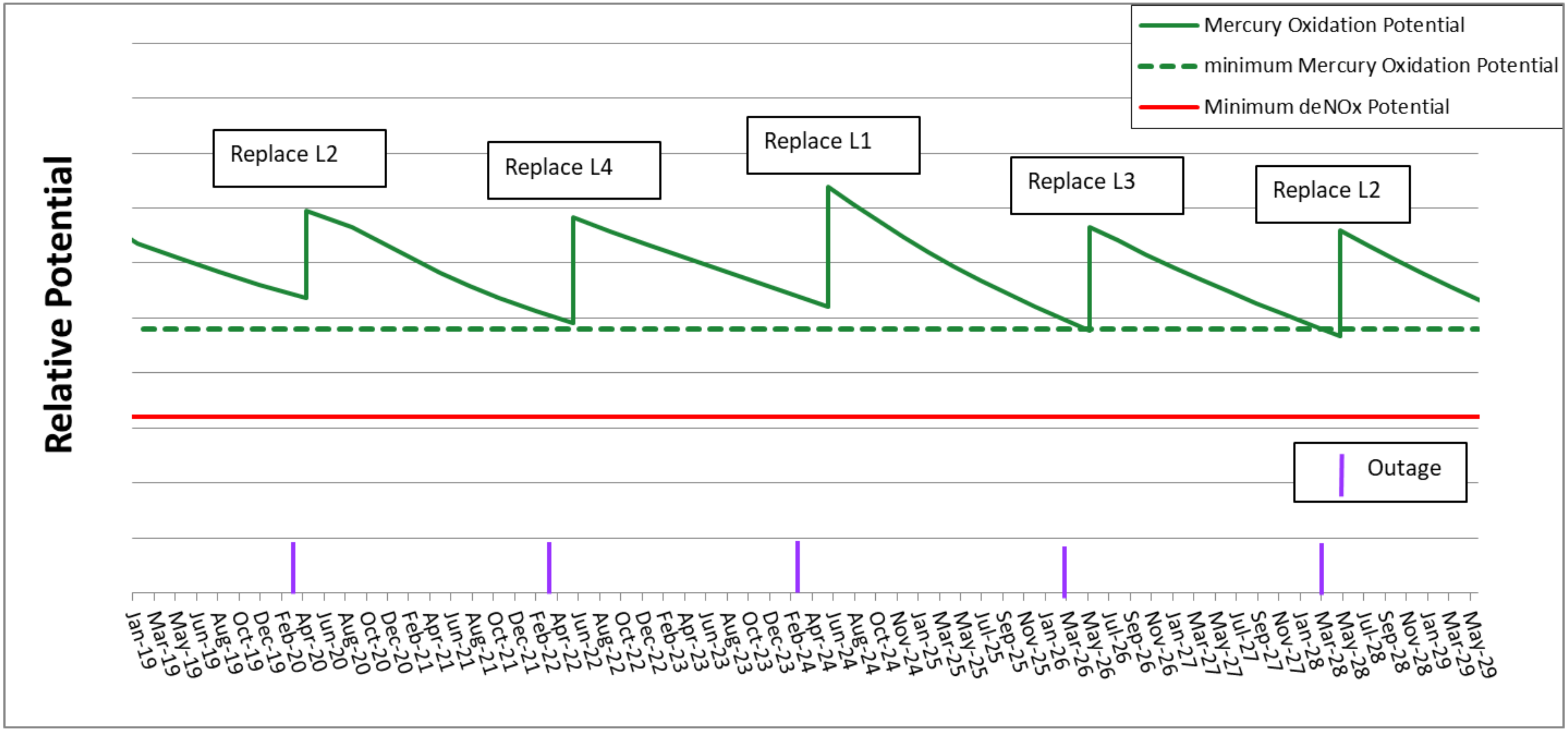
Relative Deactivation for deNOx and Mercury Oxidation

Mercury oxidation potential follows the general pattern of deNOx potential with respect to aging. Dependency on specific layer conditions will be present, especially with respect to ammonia.



Catalyst Management for Mercury Oxidation

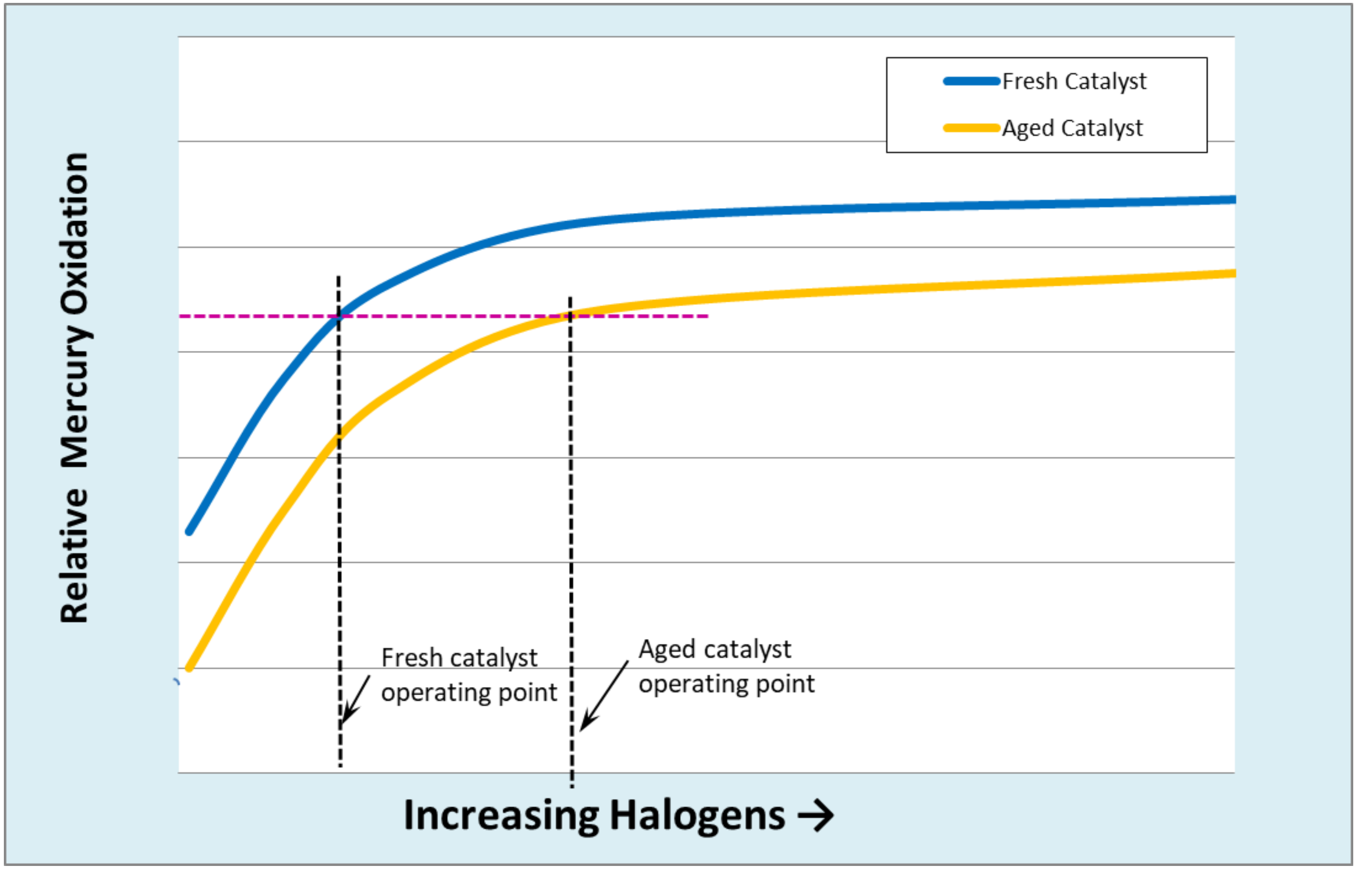
- **For certain units, the catalyst may be managed for mercury oxidation rather than deNOx, i.e. mercury oxidation is the controlling factor.**
- **In all cases a mercury oxidation rate or potential curve can be generated to compliment the deNOx potential curve.**
- **Catalyst volume and intrinsic mercury oxidation properties affect the magnitude of the step change.**



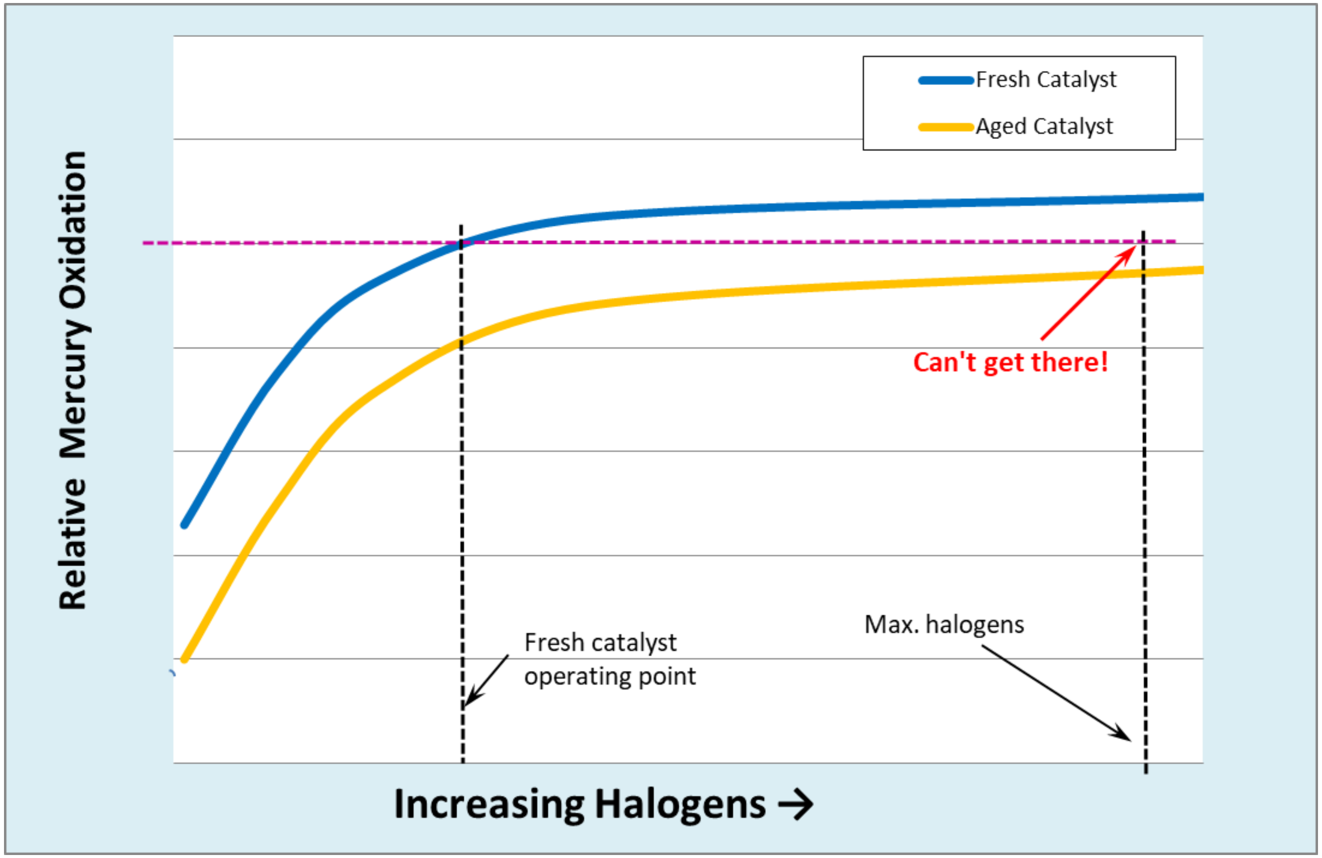
Aged Catalyst Behavior

- **Can catalyst aging be offset by adding more halogens? (maybe)**

For this case with <u>moderate</u> halogens, the catalyst aging effect <u>can</u> be compensated for with additional halogens.



For this case with <u>high</u> halogens, the catalyst aging effect <u>cannot</u> be compensated for with additional halogens.



Important Takeaways

- The entire flue gas train affects mercury oxidation and capture, be careful in isolating effects in one area and assuming that it will have a direct emissions effect.
- Additives and catalyst mercury discussions focus heavily on the SCR behavior itself, but a lot of chemistry occurs downstream, making the correspondence between the SCR behavior and overall system behavior difficult to assess and sometime counterintuitive.
- Natural fuel variability will cause variability in mercury oxidation and capture.
- Scrubber response is extremely slow, making it difficult to relate emissions effects to upstream parameters.
- There are diminishing and possibly counterproductive returns as more and more additives are injected – a balanced approach is necessary.
- Catalyst can only do so much in terms of improving mercury oxidation, an integrated approach must be taken.
- Predicting mercury oxidation behavior can be difficult. Models help tremendously to integrate all of the factors. Field data helps provide tie points. Predicting mercury behavior using a tie point, rather a priori is much easier.

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