Chemical Engineering 733
Coal Combustion

SO_2, NO_x & Mercury

06/09/22

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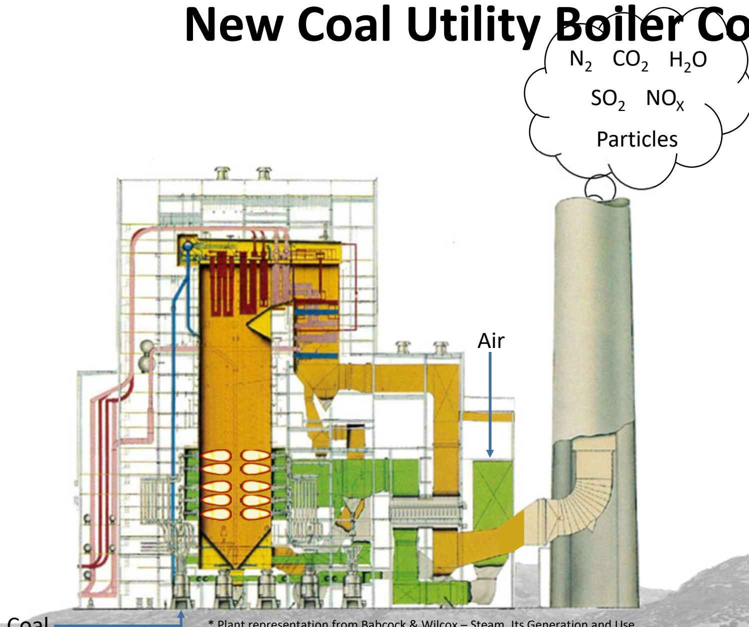
New Coal Utility Boiler Configuration



* Plant representation from Babcock & Wilcox – Steam, Its Generation and Use

Old Utility Boiler Configuration

No Air Pollution Control

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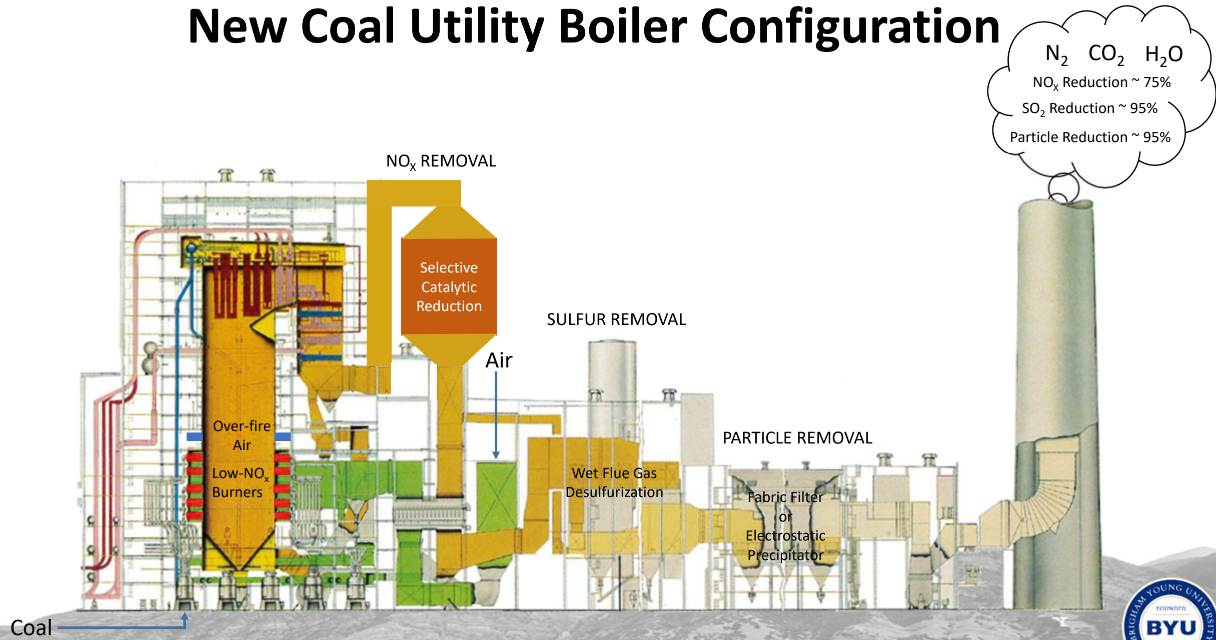
New Coal Utility Boiler Configuration



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Question 1: Describe the environmental problems associated with emission of the following chemicals (at both ground level and in the upper atmosphere). NO, NO_2, NH_3, HCN, N_2O

NOx represent a family of seven compounds. Actually, EPA regulates only nitrogen dioxide (NO_2) as a surrogate for this family of compounds because it is the most prevalent form of NOx in the atmosphere that is generated by anthropogenic (human) activities. NO_2 is not only an important air pollutant by itself, but also reacts in the atmosphere to form ozone (O_3) and acid rain.

Formula	Name	Nitrogen Valence	Properties
N_2O	nitrous oxide	1	colorless gas water soluble
NO N_2O_2	nitric oxide dinitrogen dioxide	2	colorless gas slightly water soluble
N_2O_3	dinitrogen trioxide	3	black solid water soluble, decomposes in water
NO_2 N_2O_4	nitrogen dioxide dinitrogen tetroxide	4	red-brown gas very water soluble, decomposes in water
N_2O_5	dinitrogen pentoxide	5	white solid very water soluble, decomposes in water

U.S. EPA, Clean Air Technology Center., Niotrogen Oxides (NO_x), Why and How they are Controlled. EPA-456/F-99-006R. November 1999

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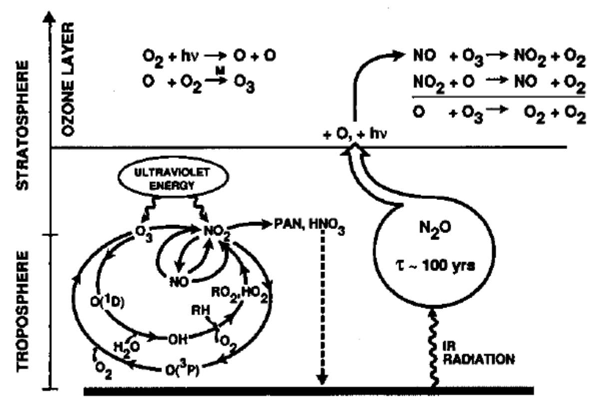

FIG. 2. The fate of nitrogen oxides in the atmosphere.[6,27]

C. Bowman, Control of combustion-generated nitrogen oxide emissions: technology driven by regulation. *Symposium (International on Combustion)*. 24(1), 1992, 859-878

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Question 2: Please discuss the different potential mechanisms of NO_x formation and destruction including: Thermal NO_x, Prompt NO_x, Fuel NO_x.

Thermal NO_x

Zeldovich Mechanism

$$O + N_2 \leftrightarrow NO + N$$
$$N + O_2 \leftrightarrow NO + O$$
$$N + OH \leftrightarrow NO + H$$

Converts molecular nitrogen from combustion air into NO

High temperature reaction, most important above 1800K
This is because the first reaction has a high activation energy

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Prompt NO_x

Fenimore Mechanism

$$CH + N_2 \leftrightarrow HCN + N$$
$$C + N_2 \leftrightarrow CN + N$$

Converts molecular nitrogen from combustion air into cyano compounds through attack by hydrocarbon fragments

Fuel rich reaction

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Fuel NO_x

Oxidation of nitrogen originating in the fuel molecular structure

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Prompt and Fuel NO_x

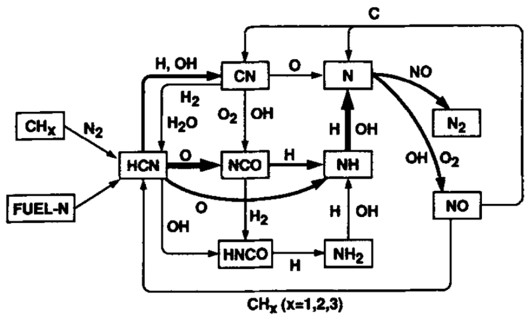

FIG. 3. Reaction path diagram illustrating the major steps in prompt NO formation, the conversion of fuel nitrogen in flames, and reburning.[33]

C. Bowman, Control of combustion-generated nitrogen oxide emissions: technology driven by regulation. *Symposium (International on Combustion)*. 24(1), 1992, 859-878

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Have a look at GRI Mech 3.0

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Question 3: Please discuss how nitrogen is released from coal during (a) devolatilization and (b) char oxidation. (You may have to look earlier in the NO_x chapter in the red book (Pages 450-456).

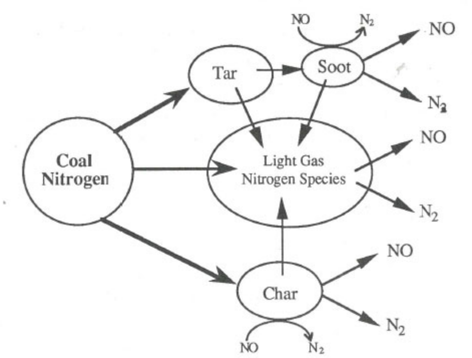

Fig. 6.2 Fuel nitrogen pathways leading to nitrogen pollutant formation during coal combustion.

L.D. Smoot, Fundamentals of Coal Combustion for Clean and Efficient Use. *Elsevier,* 1993

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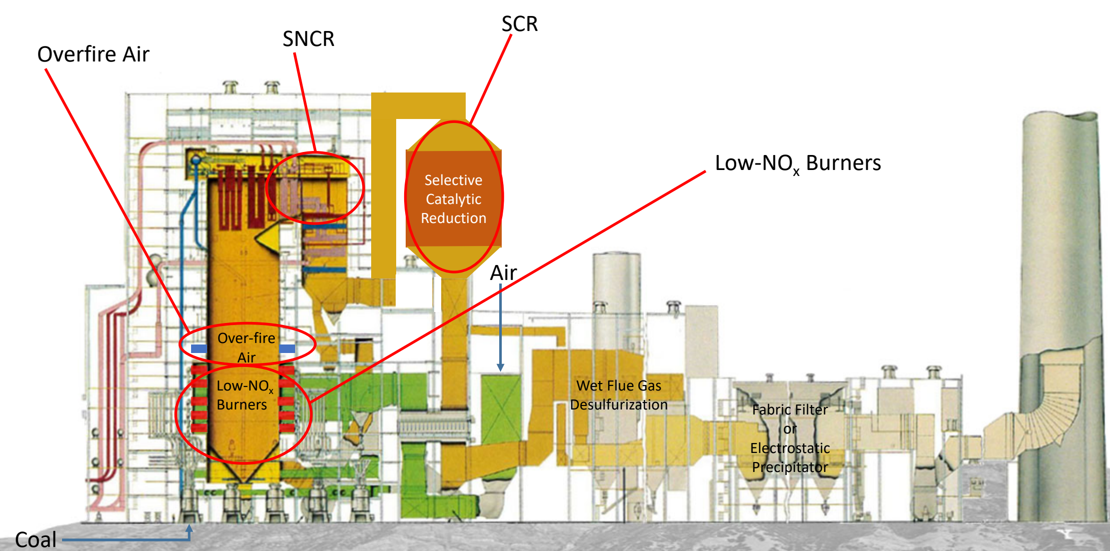
Question 4: Describe the following process NO_x control strategies: Low excess air, Low NO_x burners, Overfire air, Reburning, SNCR (selective non-catalytic reduction), SCR (selective catalytic reduction).



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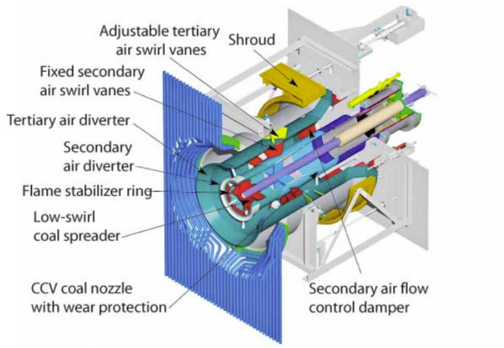
Low-NO_x Burners (LNB), usually installed with Over-fire Air (OFA)



~ 50% reduction in NO_x

~ $75 Million Capital Investment for Hunter, Unit 3

A. Bodnarik, ICI Boiler NO_x & SO_2 Control Cost Estimates. *OTC Committee Meeting, Modeling/Stationary & Area/Mobile Sources, Niagra Falls, NY, Sept. 2009*

Pollution Control: Low-NO_x Combustion Retrofit Options. *Power,* May 2007

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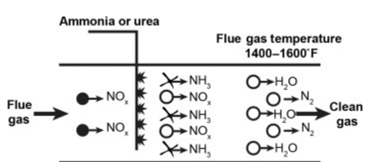
Selective Non-catalytic Reduction (SNCR)



~ 45% reduction in NO_x

~ $140 Million Capital Investment for Hunter, Unit 3

A. Bodnarik, ICI Boiler NO_x & SO_2 Control Cost Estimates. *OTC Committee Meeting, Modeling/Stationary & Area/Mobile Sources, Niagra Falls, NY, Sept. 2009*

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

$$4NO + 2CO(NH_2)_2 + O_2 \rightarrow 4N_2 + 2CO_2 + 6H_2O$$

B. Miller, Formation and Control of Nitrogen Oxides. *Clean Coal Engineering Technology (Second Edition), 2017*

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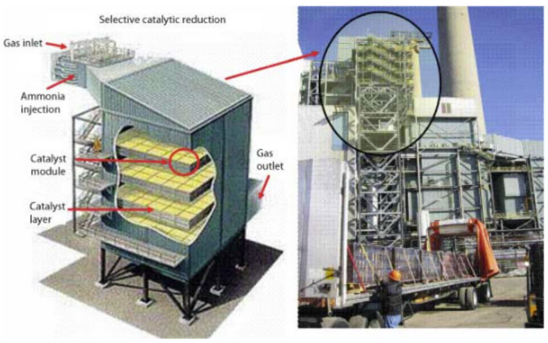
Question 4: Describe the following process NO_x control strategies: Low excess air, Low NO_x burners, Overfire air, Reburning, SNCR (selective non-catalytic reduction), SCR (selective catalytic reduction).

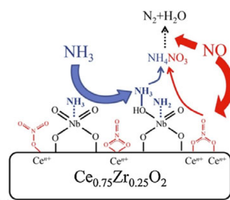
Selective Catalytic Reduction (SCR)



~ 85% reduction in NO_x

~ $280 Million Capital Investment for Hunter, Unit 3

A. Bodnarik, ICI Boiler NO_x & SO_2 Control Cost Estimates. *OTC Committee Meeting, Modeling/Stationary & Area/Mobile Sources, Niagra Falls, NY, Sept. 2009*



Environmentally Sound Handling of Deactivated SCR Catalyst. *Power,* July 2008

Z. Ma, X. Wu, H. Härelind, D. Wang. B. Wang, Z. Si., NH_3-SCR reaction mechanisms of $NbO_x/Ce_{0.75}Zr_{0.25}O_2$ catalyst: DRIFTS and kinetics studies. *Journal of Molecular Catalysis A: Chemical,* 423, 2016, 172-180

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Question 5: Describe the costs (relative to each other) of each of the NO_x control strategies in question 4. Which strategies are generally used for retrofits on old boilers, rather than on new boilers?

See Previous Slides

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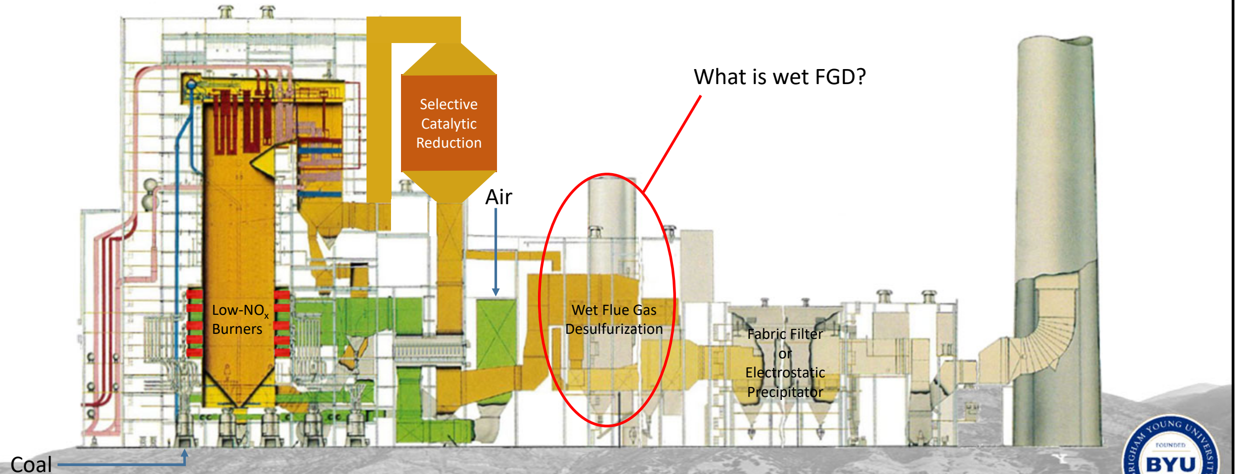
What about SO_2?



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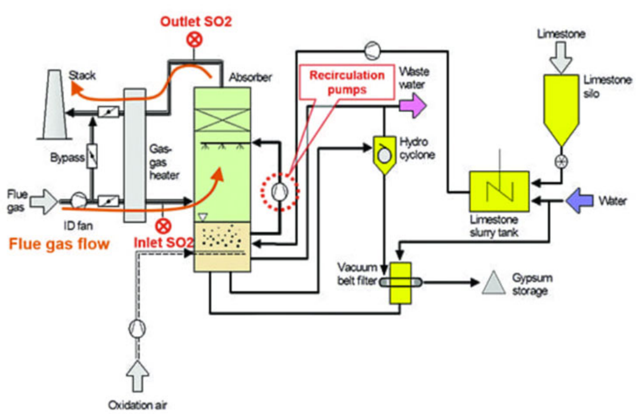
What about SO_2?



~ 90% reduction in NO_x

~ $180 Million Capital Investment for Hunter, Unit 3

J. Cichanowicz, Current Capital Cost and Cost-effectiveness of Power Plant Emissions Control Technologies. *Utility Air Regualtory Group Report, EPA-R08-OAR-2012-0026-0241, 2010*

$$CaCO_3 + SO_2 + 2H_2O + {}^{1}\!/_{2}\, O_2 \leftrightarrow CaSO_4 + 2H_2O + CO_2$$

Advanced Process Control for Optimizing Flue Gas Desulfurization. *Power,* Nov. 2018

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Mercury Chemistry

Mercury Speciation

- Hg^0 – Elemental Hg

Remains in the gas phase, not capturable

- Hg^{+2} – Oxidized forms of Hg (Predominantly $HgCl_2$, $HgBr_2$)

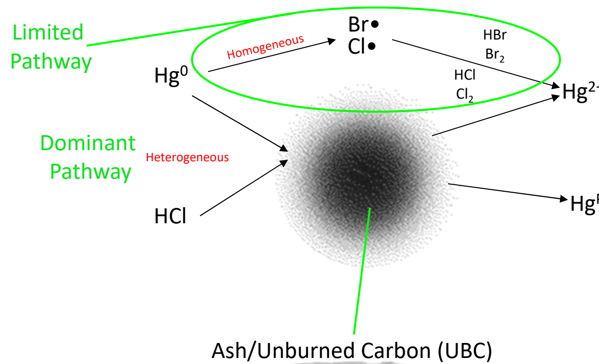
Water Soluble, Easy to capture

- Hg^P – Particulate-bound Hg

Removed with particulate

- $Hg^{Total(T)} = Hg^P + Hg^{+2} + Hg^0$
- $Hg^{Total\ Gaseous\ (TG)} = Hg^{+2} + Hg^0$

Mercury Reaction Pathways



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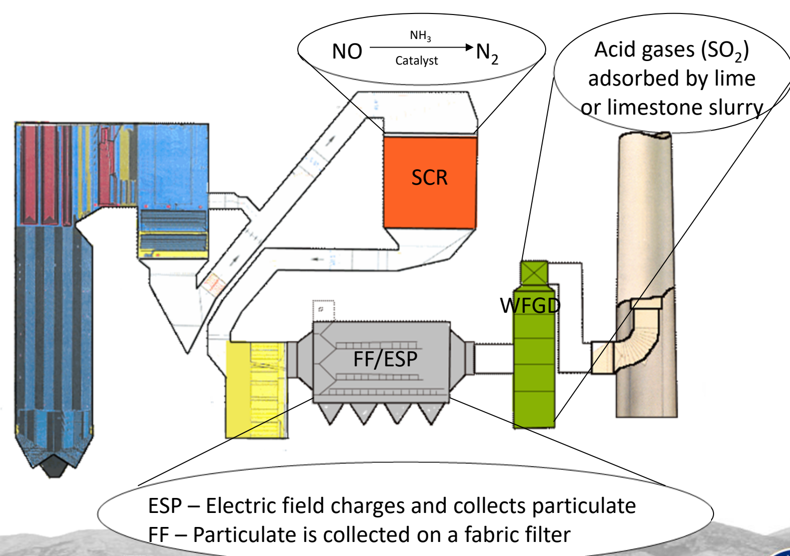
Mercury Behavior in a Coal Power Station



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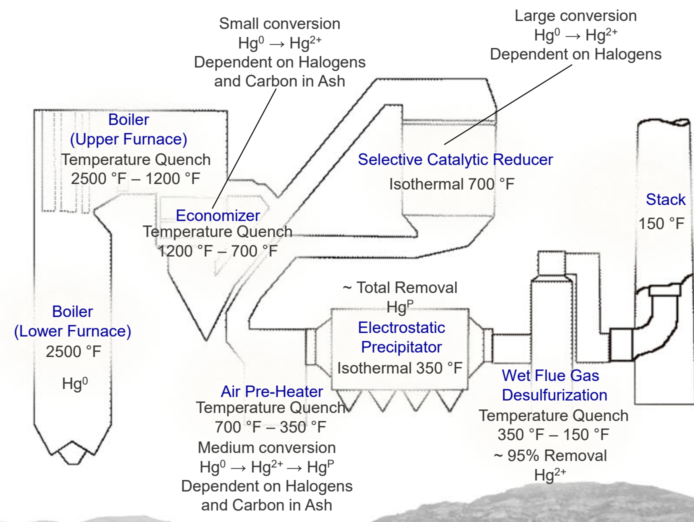

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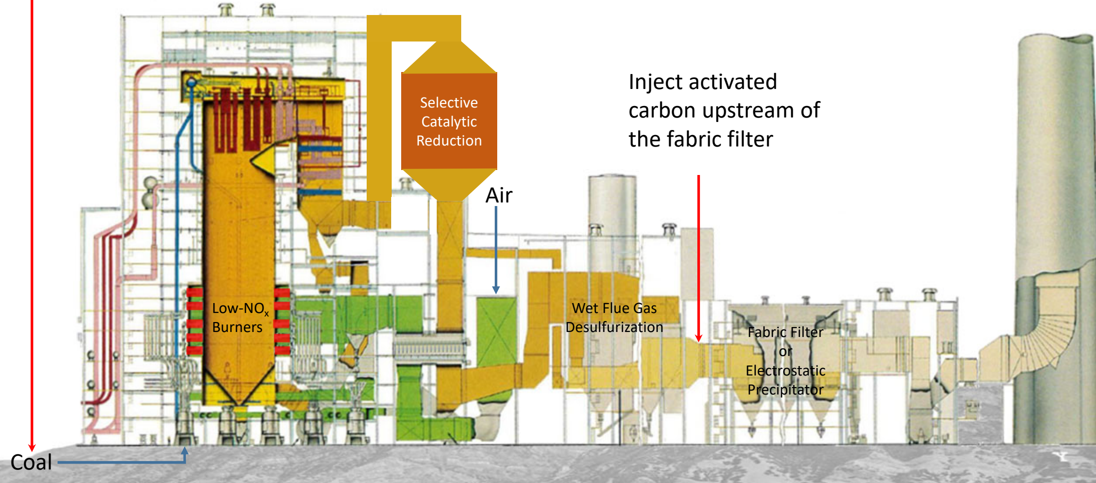
Mercury Control

Inject halogen salts with/on the fuel



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