System for the Removal of NO_X and SO_2 from Incinerator Effluents

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Overview

- **Need for waste incineration in long term life support systems.**
  - Inhabitation of Lunar or Martian surface.
- **Generation of NO_x and SO_x in incinerators.**
- **Technology to control NO_x and SO_x.**
- **NO_x control by oxidation and scrubbing.**
- **SO_x removal.**
- **Results obtained in Phase I.**
- **Proposed work in Phase II.**

Waste Incineration in Long Term Life Support Systems

- **Eliminates the hazards and difficulties associated with storing wastes.**
- **Converts waste to carbon dioxide, water, and ash, which are used to regenerate food supply.**
- **Unfortunately, incineration also produces toxic compounds.**
  - NO and NO_2 (NO_x).
  - SO_2.
  - CO, hydrocarbons.

NO_x and SO_2 Generation in Combustion

- **At high temperatures, thermodynamics strongly favor NO and SO_2.**
- **At these temperatures, kinetics are rapid.**
- **Sources of nitrogen are the air used in combustion and nitrogen containing compounds in material burned.**
- **Sulfur comes from material burned.**

Current Control Technology

- **NO_x control in net oxidizing environments.**
  - Selective Reduction (catalytic and non catalytic).
    - Reducing agent must react with NO instead of O_2.
    - $3\ NO + 2\ NH_3 \rightarrow 5/2\ N_2 + 3\ H_2O$.
  - Combustion modification (reduce temperature).
  - Catalysts for direct decomposition of NO into N_2 and O_2 are poisoned by oxygen.
- **SO_x control.**
  - Wet or dry adsorption with basic compound such as CaO, or $CaCO_3$.

Problems with Selective Reduction for NO_x Control

- **Reaction requires addition of ammonia.**
  - Must be present in <u>excess</u> to achieve high efficiency.
- **Difficult to inject so that it is well mixed prior to contacting catalyst.**
  - (Non catalytic systems suffer from poor efficiency).
- **Instrumentation required to adjust NH_3 injection to changing NO concentrations.**
- **Handling ammonia can be dangerous, requires pressurized tank.**

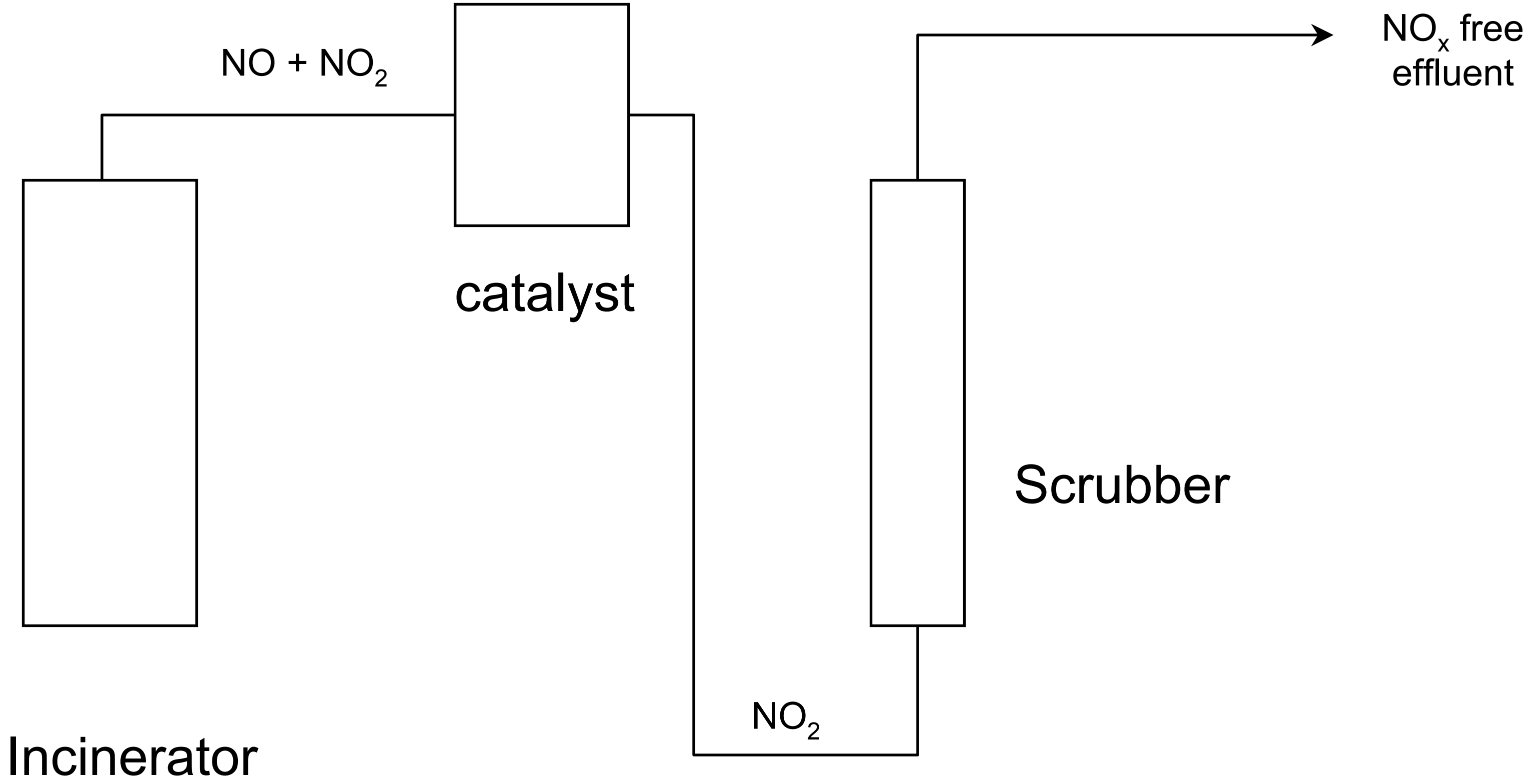
NO_x Removal by Oxidation and Scrubbing

- Take advantage of excess oxygen in effluent stream to catalytically oxidize NO to NO_2 (NO is not soluble in aqueous solutions).
- NO_2 is very soluble in water forming HNO_2 and HNO_3 which can be neutralized by basic solutions such as $NaHCO_3$.

Advantages of NO_x Removal by Oxidation and Scrubbing over SCR

- Does not require addition of reactant prior to contacting catalyst.
- Does not require instrumentation to constantly adjust concentration of NH_3.
- Does not require use of toxic compound in pressurized tank.
- No potential for exposing crew to ammonia.

Schematic of System



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Chemical Reactions

- **Oxidation**
  - $NO + 1/2\ O_2 \rightarrow NO_2$
  - Occurs rapidly on catalyst, slowly in air.
- **Adsorption and neutralization of NO_2**
  - $2\ NO_2 + H_2O \rightarrow HNO_3 + HNO_2$
  - $HNO_3 + Na^+ + HCO_3^- \rightarrow H_2CO_3 + Na^+ + NO_3^-$
  - $H_2CO_3 \rightarrow CO_2 + H_2O$
- **NO_2 can be converted into harmless salt with benign base. Base is not affected by CO_2.**

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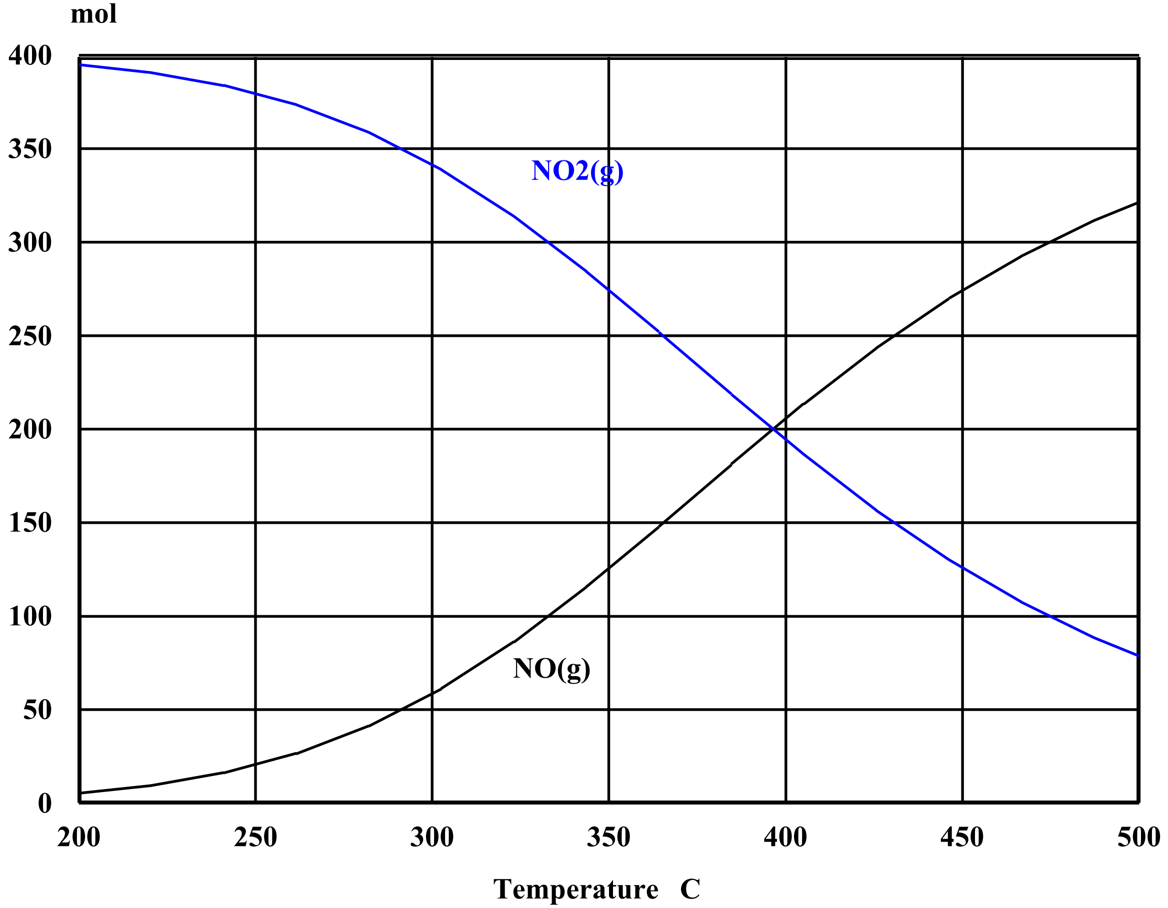
Thermodynamics require NO Oxidation at Low Temperature



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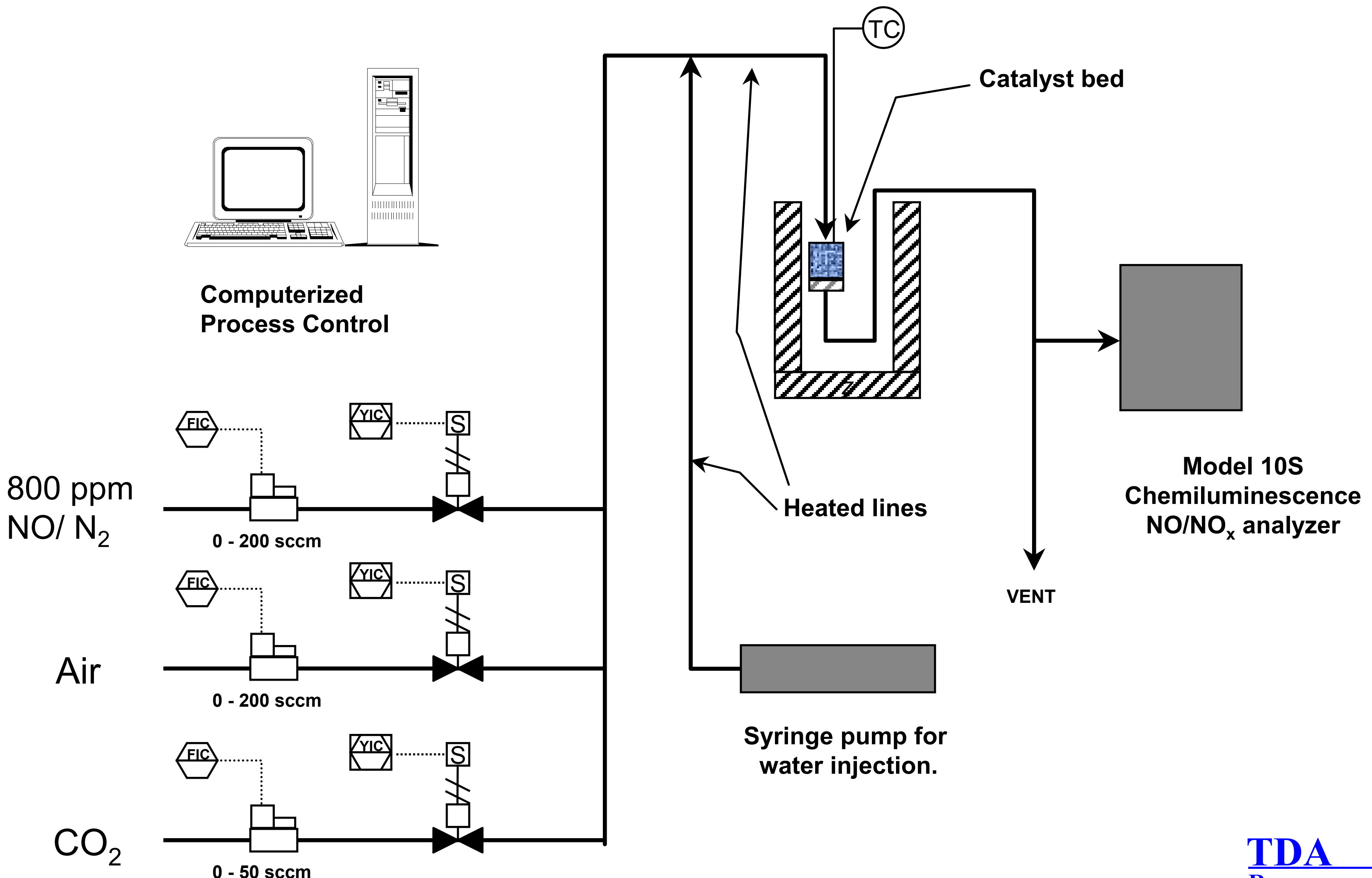
TDA Phase I Project

- **Optimize catalysts for NO oxidation.**
  - Test catalysts consisting of transition metal oxides for NO oxidation activity.
  - 365 ppm NO, 10% CO_2, 8% H_2O, 10% O_2.
- **Determine efficiency of scrubber for removal of NO_x.**
- **Measure scrubber efficiency for SO_2 removal.**

Experimental Apparatus



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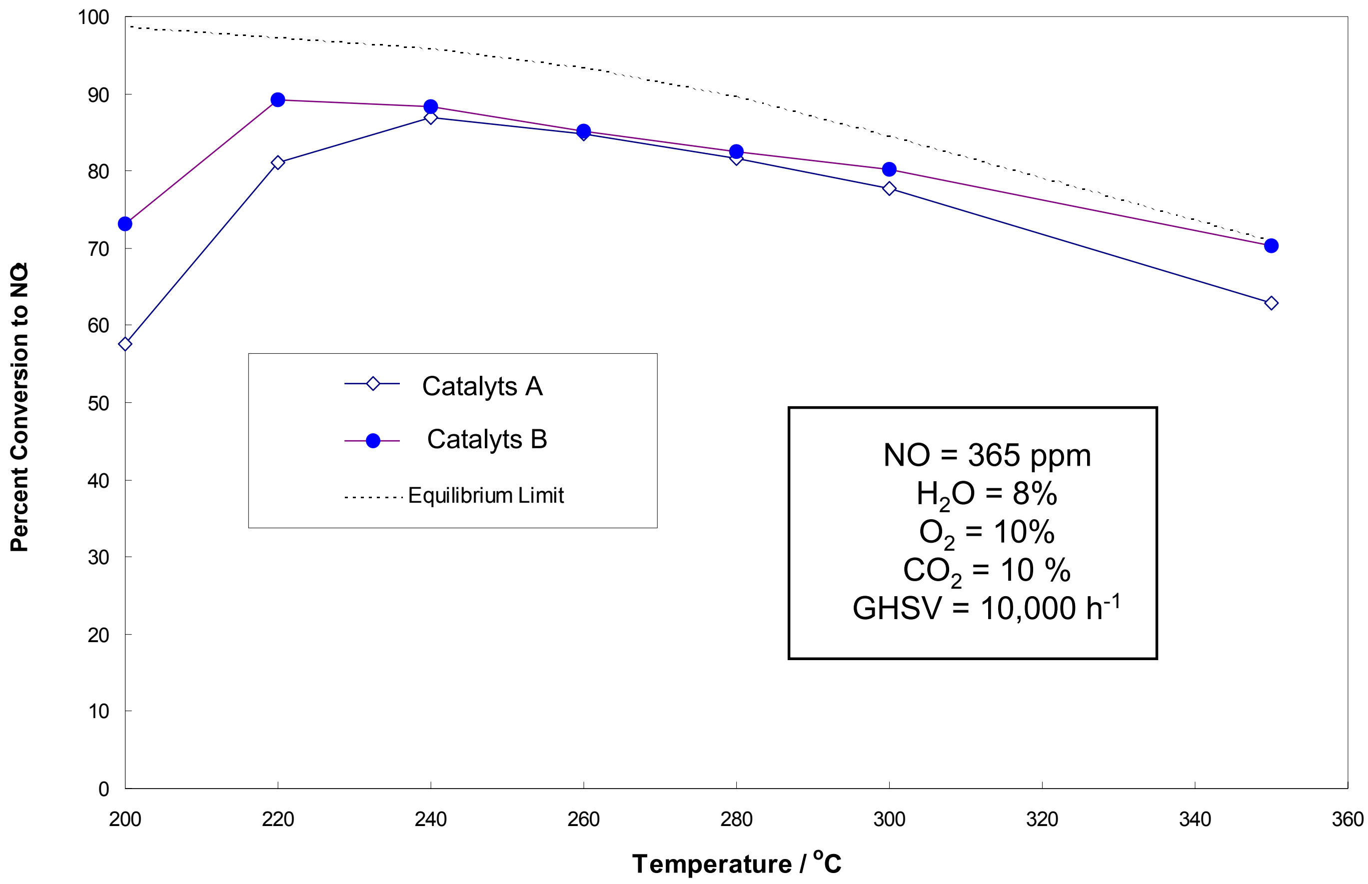
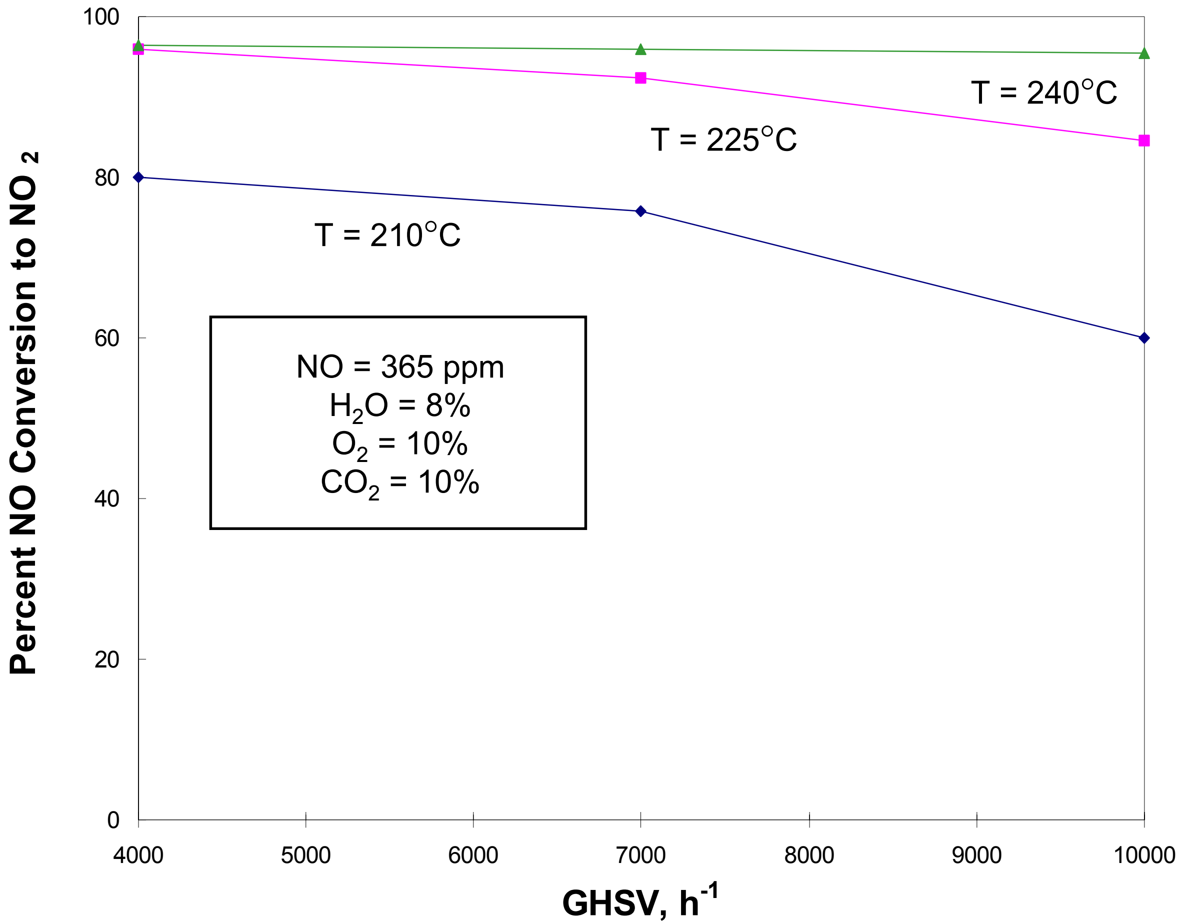
NO Oxidation Tests

- Pretreat catalyst at 350°C for 1 h in mixture of NO, CO_2, and O_2.
- Temp 350°C; 365 ppm NO, 10% CO_2, 8% H_2O, 10% O_2, balance N_2.
- Flow = 10,000 sccm/g catalyst per hour.
- Measure conversion to NO_2.
- Repeat measurements at 20°C intervals to 200°C.

Results of Catalyst Screening Tests



Optimum Temperature for NO Oxidation is 240°C



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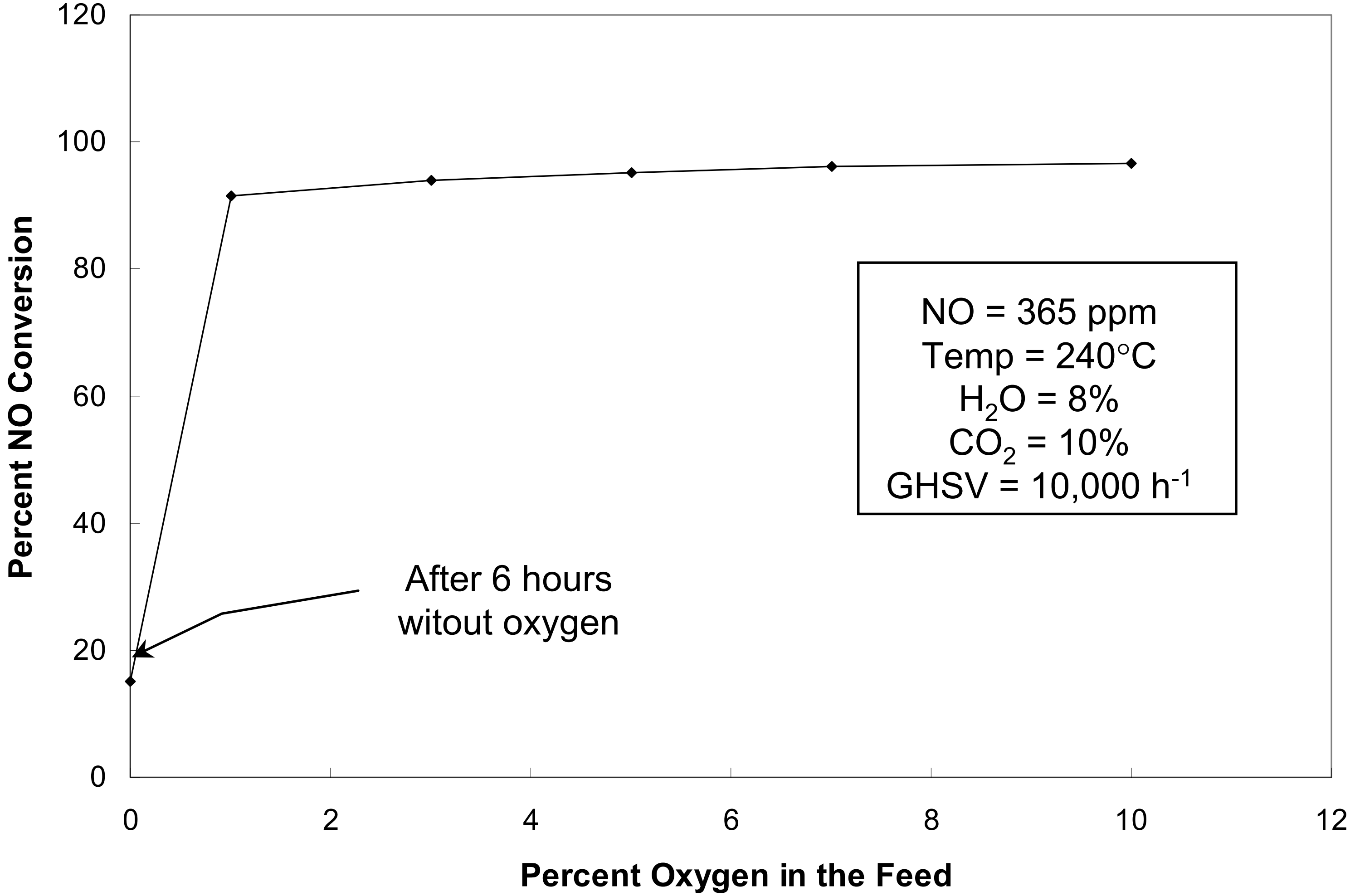
Conversion is Constant at Oxygen Concentrations > 1%



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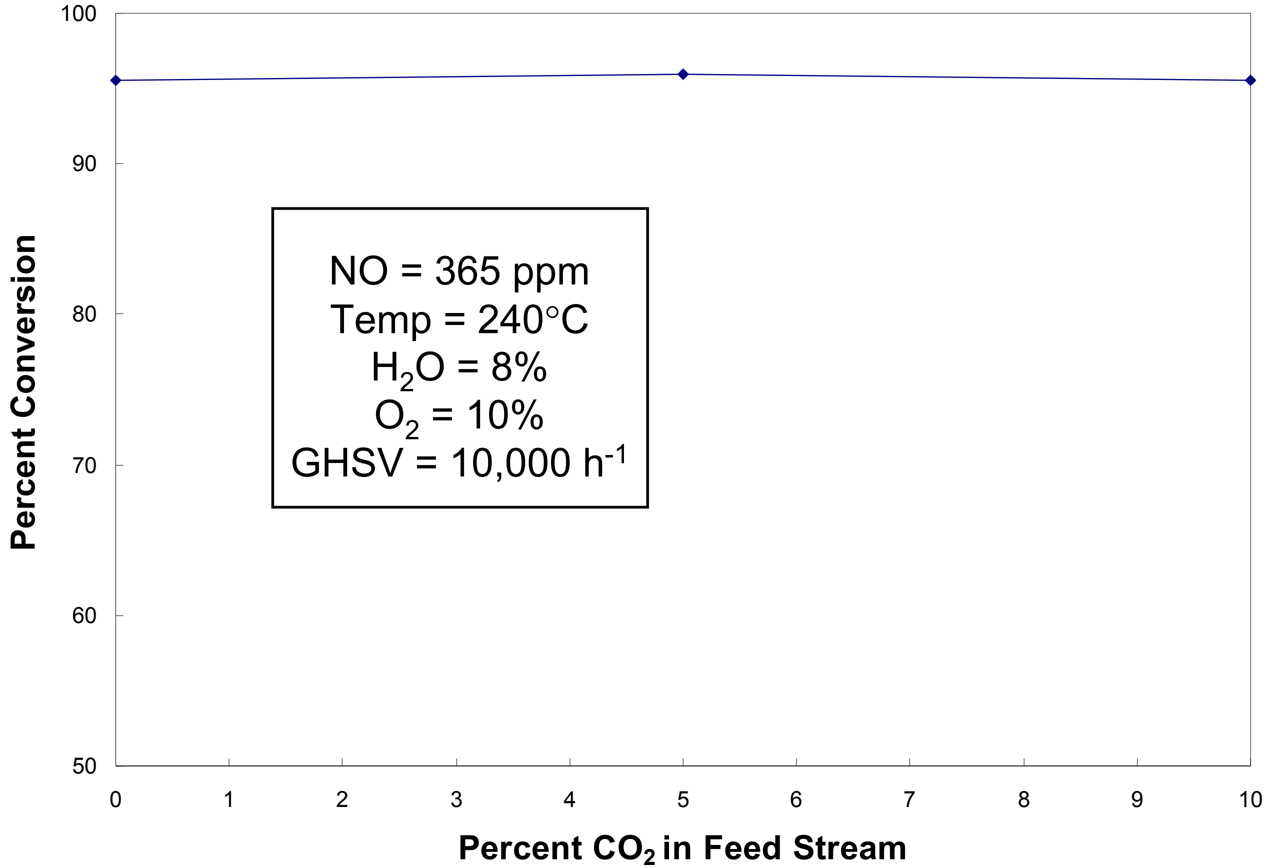
NO Conversion not Affected by CO_2



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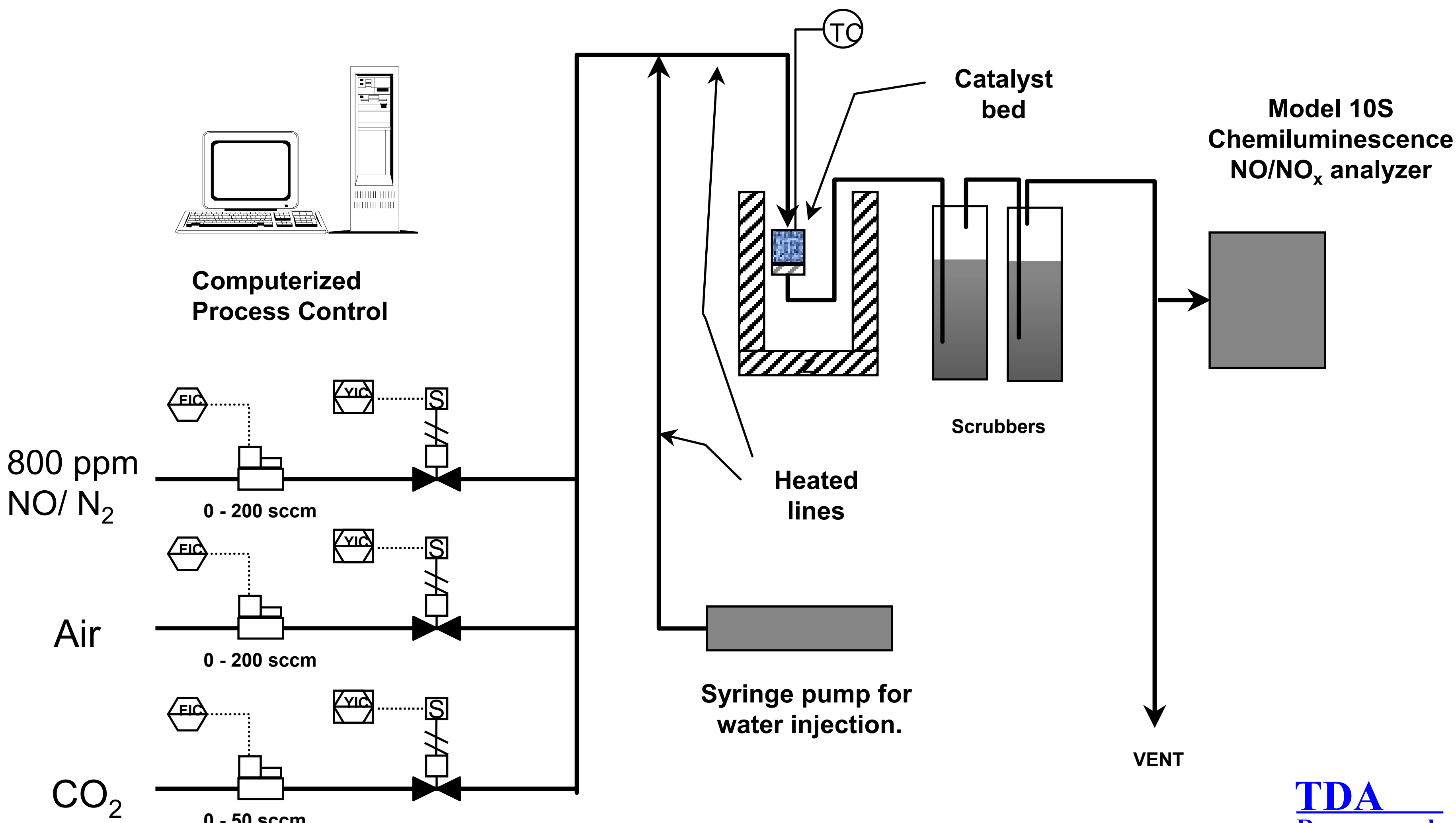
Overall NO_x Removal by Oxidation and Scrubbing

- NO, air, and CO_2 passed over Co_3O_4 catalyst maintained at 240°C.
- Up to 48% water added to feed stream.
- Flow exiting catalyst is passed through two scrubbers containing 0.5 M sodium bicarbonate solution.
- Flow exiting scrubbers is directed into NO_x analyzer.

Experimental Apparatus with Scrubbers



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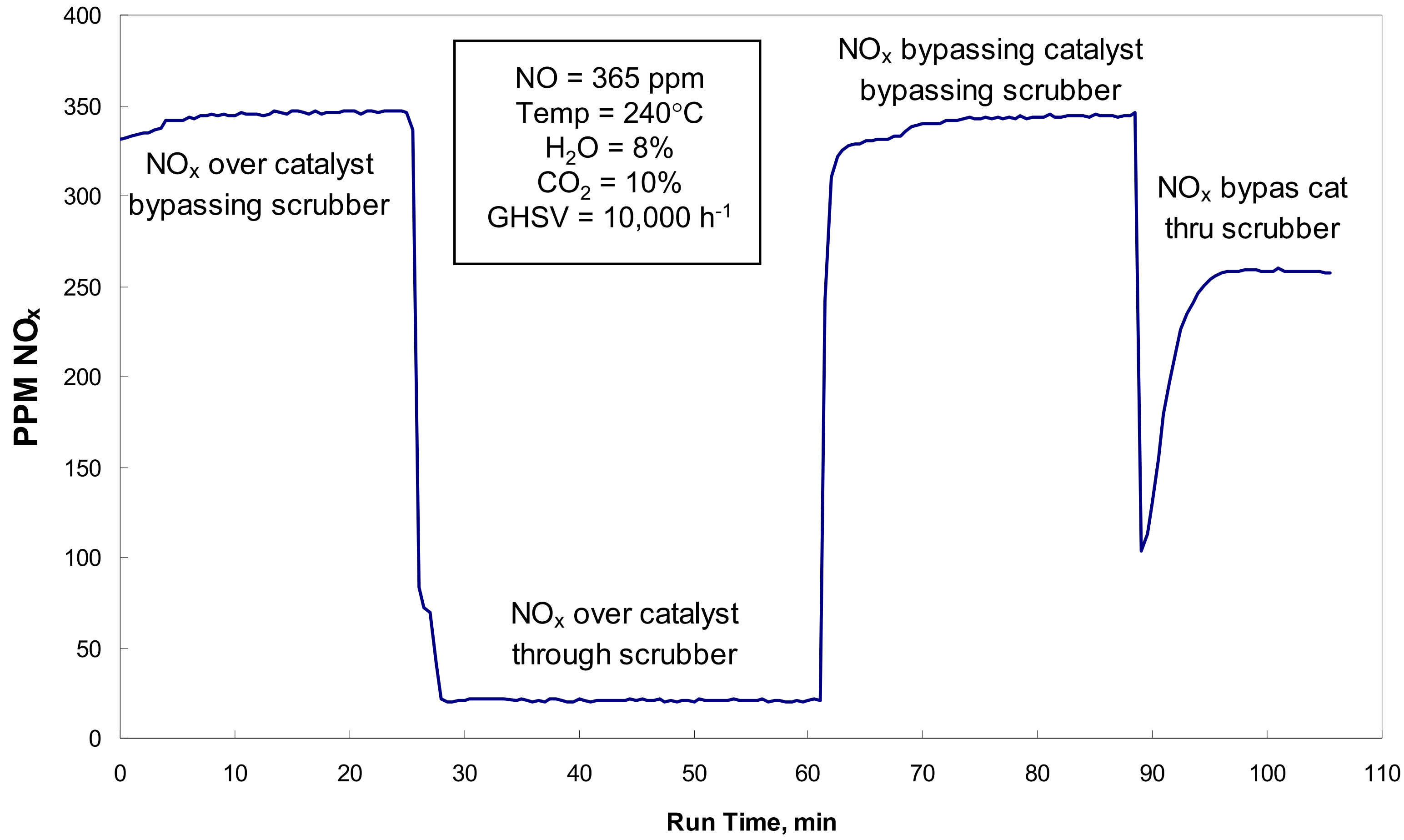
High NO_x Removal Efficiency with Catalvst and Scrubber



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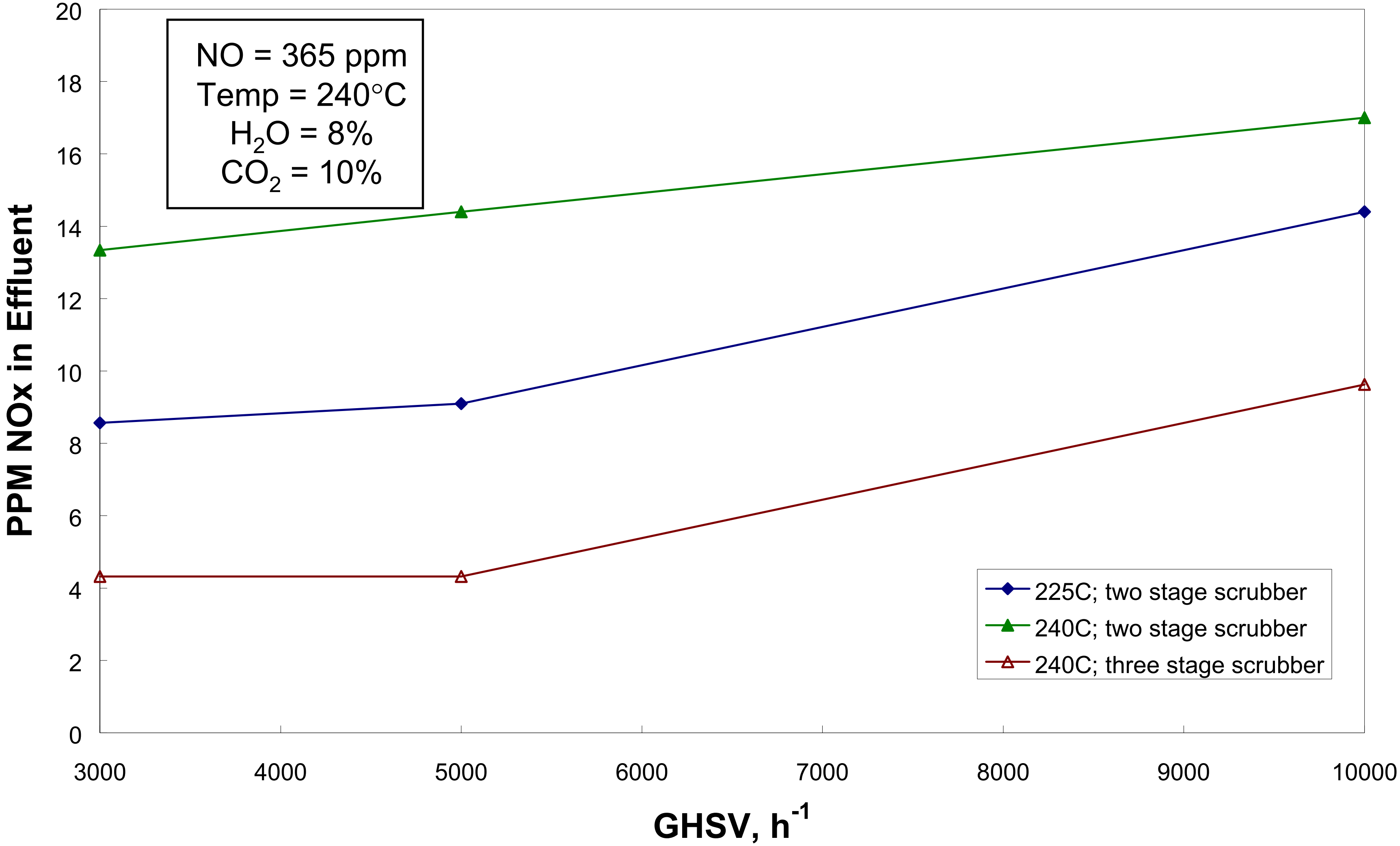
Optimization of NO_x Removal from Effluent



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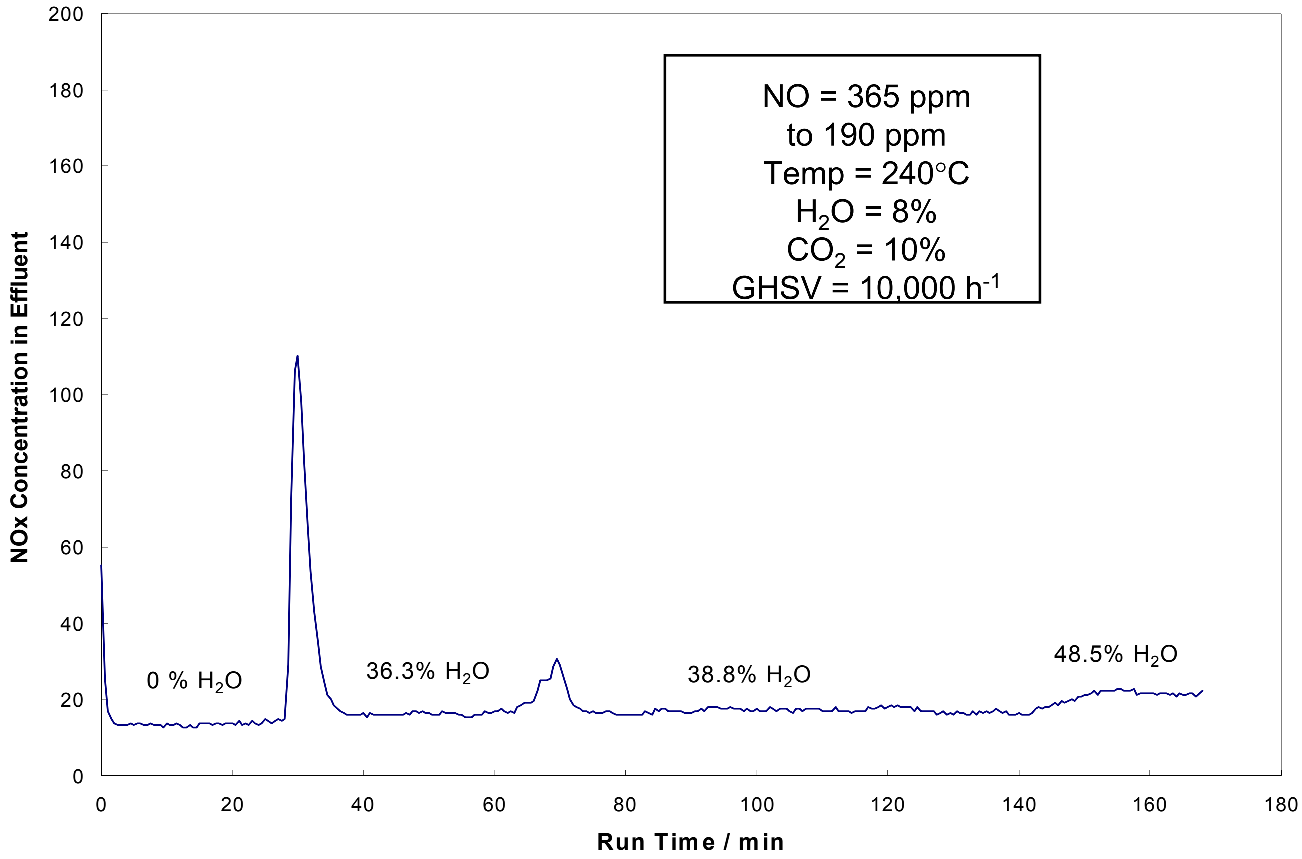
NO_x Removal not Affected by High Water Concentrations



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Sulfur Dioxide Removal

- **Commercial methods have been developed to remove SO_2 from flue gas for coal fired power plants - for example:**
  - Wet scrubbing (e.g $CaCO_3$ slurries)
  - Dry scrubbing (e.g Na_2CO_3 injection)
- **Our choice**
  - Fixed Bed - Na_2CO_3 absorber

$$SO_2(g) + 1/2\ O_2\ (g) + Na_2CO_3 \rightarrow Na_2SO_4 + CO_2(g)$$

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SO_2 Removal with a Fixed Bed of Na_2CO_3

- **Advantages**
  - Mechanically simple
  - High capacity (0.6g SO_2/g Na_2CO_3 from reaction stoichiometry)
  - Reaction is thermodynamically irreversible at temperatures of interest (300 - 600°C)
  - Unaffected by presence of CO_2
  - Water (steam) and air (O_2) that will be present in combustor flue gas will improve sorbent performance
- **Disadvantages**
  - Non-regenerable

Preliminary Bed Design

- **Input parameters (pre-experiment calculations).**
  - Particle diameter = 0.5 mm.
  - Bed diameter = 1.5 in.
  - Gas flow 700 sccm.
  - Temperature = 300°C.
  - Bed void fraction ε = 0.4.
  - Used density and viscosity of air @ 300C & 1 atm.
- **Mass transfer coefficient.**
  - Chapman-Enskog for diffusivity (D_{AB}) of SO_2 in air.
  - Assumed effective diffusivity in bed = 10% $D_{AB.}$
  - Chilton-Colburn factor j_D to calculate k.

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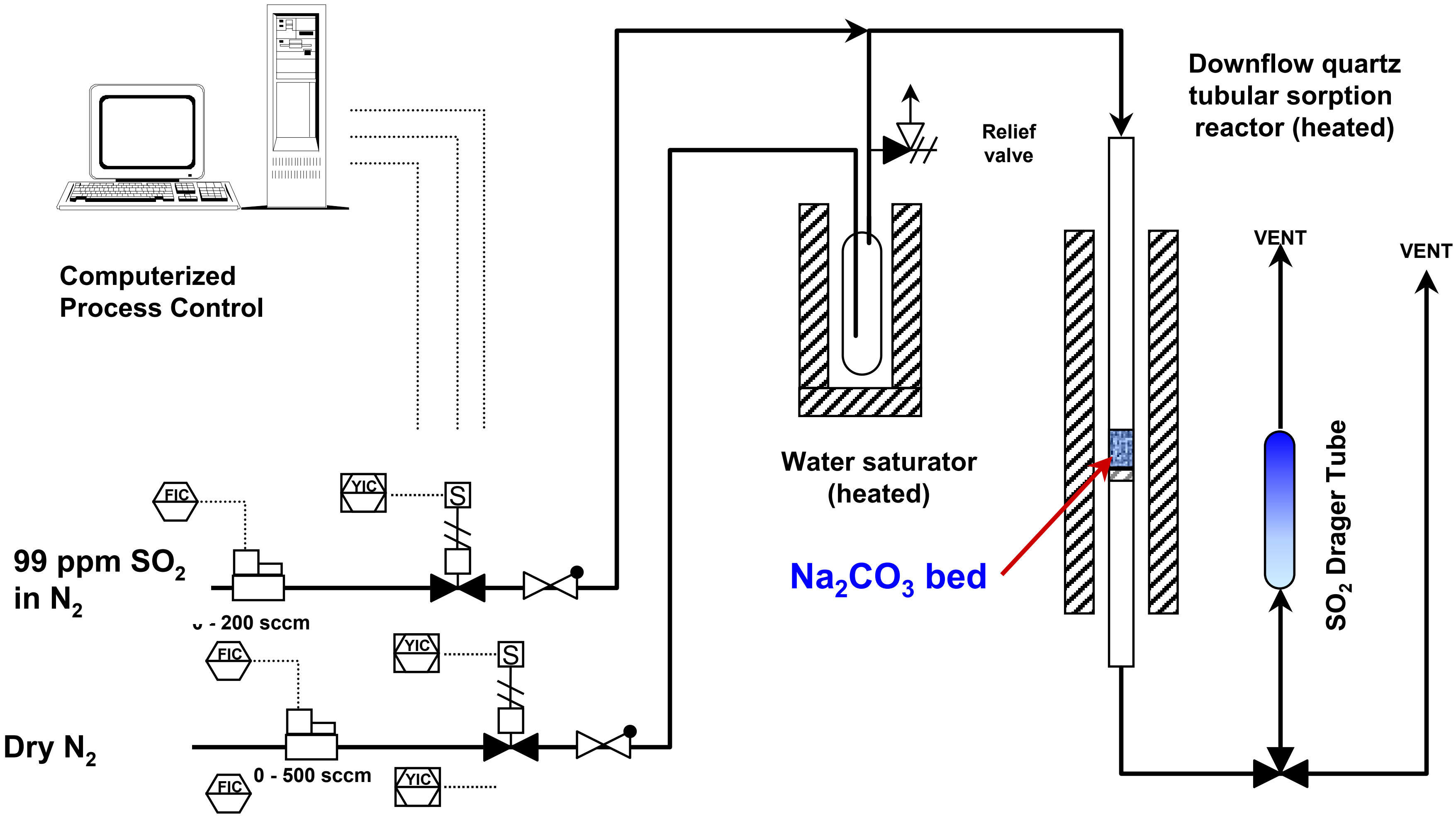
SO_2 Sorption Apparatus



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SO_2 Sorption Experiment

- **Goal - validate basic design approach.**
- **Performed fixed Na_2CO_3 bed sorption experiments.**
  - Inlet SO_2 concentration = 28 ppm.
  - Water concentration 37.5 vol %.
  - Balance $N_{2.}$
  - Temperature 300°C.
  - SO_2 detection with Drager Tubes (colorimetric).
- **Model predicts SO_2 breakthrough at 25 hours.**

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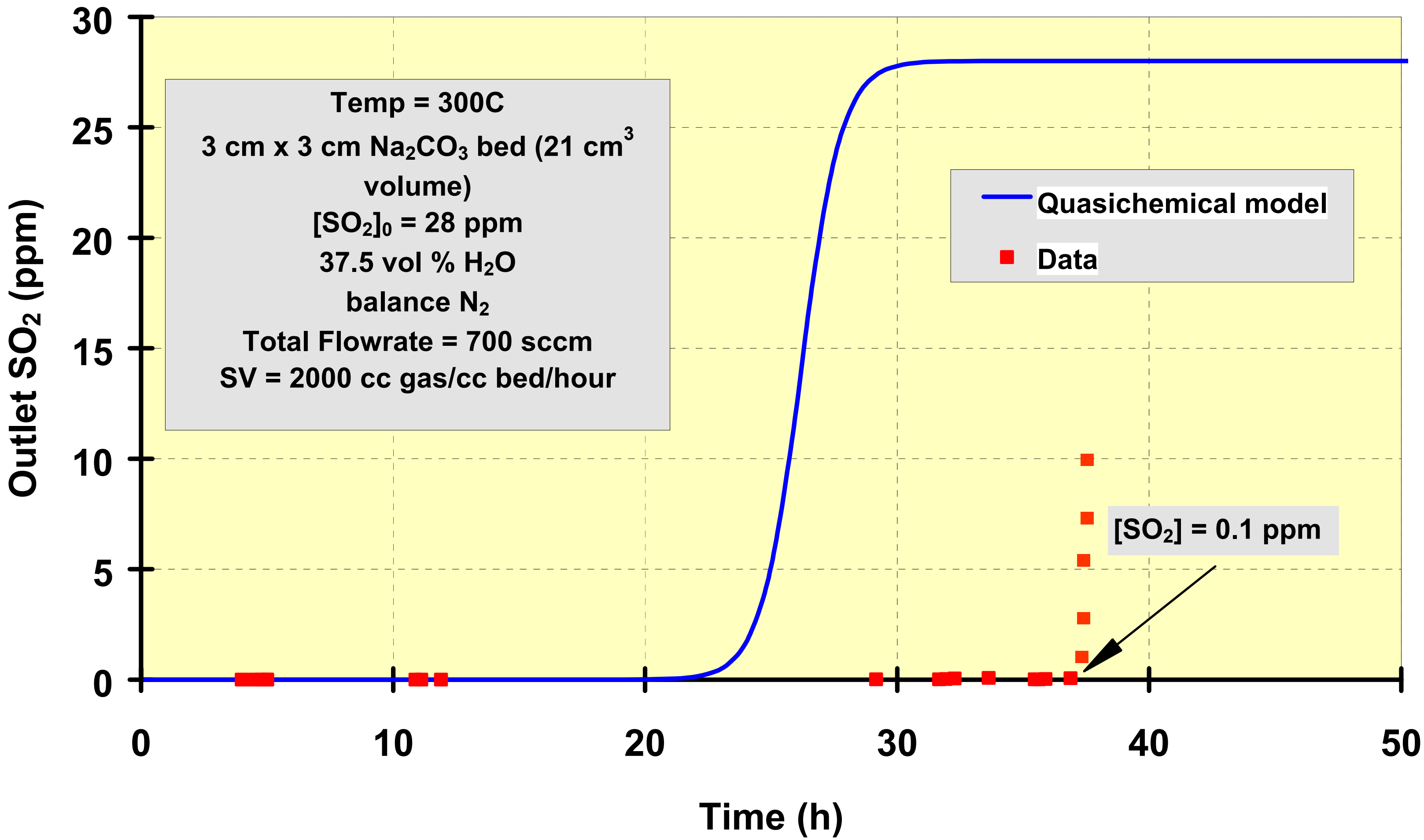
SO_2 Removal by Absorption with Na_2CO_3

Predicted vs. Experimental Data



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Phase II Project

- **Design and construct system to control all hazardous components from NASA Ames incinerator effluent.**
  - NO_x, SO_2, CO, hydrocarbons, HCl.
- **Test system on fluidized bed Combustor at NASA Ames Research Center.**
  - Typical operating conditions*
    - Feed rate 700 - 800 g/hr
    - Air flow - 62 standard liters/minute
    - Bed temperature ca. 1100K +
    - Pressure ca. 1 atm

* Fisher et al. SAE 981758

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Summary and Conclusions

- Demonstrated that NO_x can be controlled by oxidation and wet scrubbing.
- Over 95% removal efficiency obtained in the presence of oxygen. Water has little effect on effluent concentration.
- Does not require addition of dangerous reagent or use of complicated injection system and monitoring equipment.

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Summary and Conclusions

- SO_2 can be controlled by adsorption with Na_2CO_3.
- Achieved over 99.5% removal after 35 h of operation.
- In Phase II TDA will design and construct an integrated system for control of NO_x, SO_2, HC's, CO.

Acknowledgements

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