

Experimental Results Obtained with a Pilot Scale System to Remove Pollutants from an Incinerator Effluent

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Overview

- **Phase II objective.**
- **Design of the full scale system.**
- **SO₂ sorbent**
- **NO oxidation catalyst.**
- **NO₂ scrubbers.**
- **Overall performance of the unit.**

Phase II Objective

- **Design and construct a waste treatment system for use on the NASA Ames incinerator.**
- **Carry out laboratory tests to size components.**
- **Construct and test pilot scale components.**
- **Assemble and deliver the system.**

Incinerator Effluent Composition*

| Component | Concentration | Kg/h |
|------------------------------|---------------|--------|
| N ₂ | 34% | 4.22 |
| O ₂ | 6% | 0.19 |
| CO ₂ | 10% | 1.06 |
| H ₂ O | 49% | 4.26 |
| HC (CO) | 1% | 0.03 |
| SO ₂ [†] | 100 ppm | 0.0005 |
| NO _x | 400 ppm | 0.0005 |
| Ash | | 0.001 |

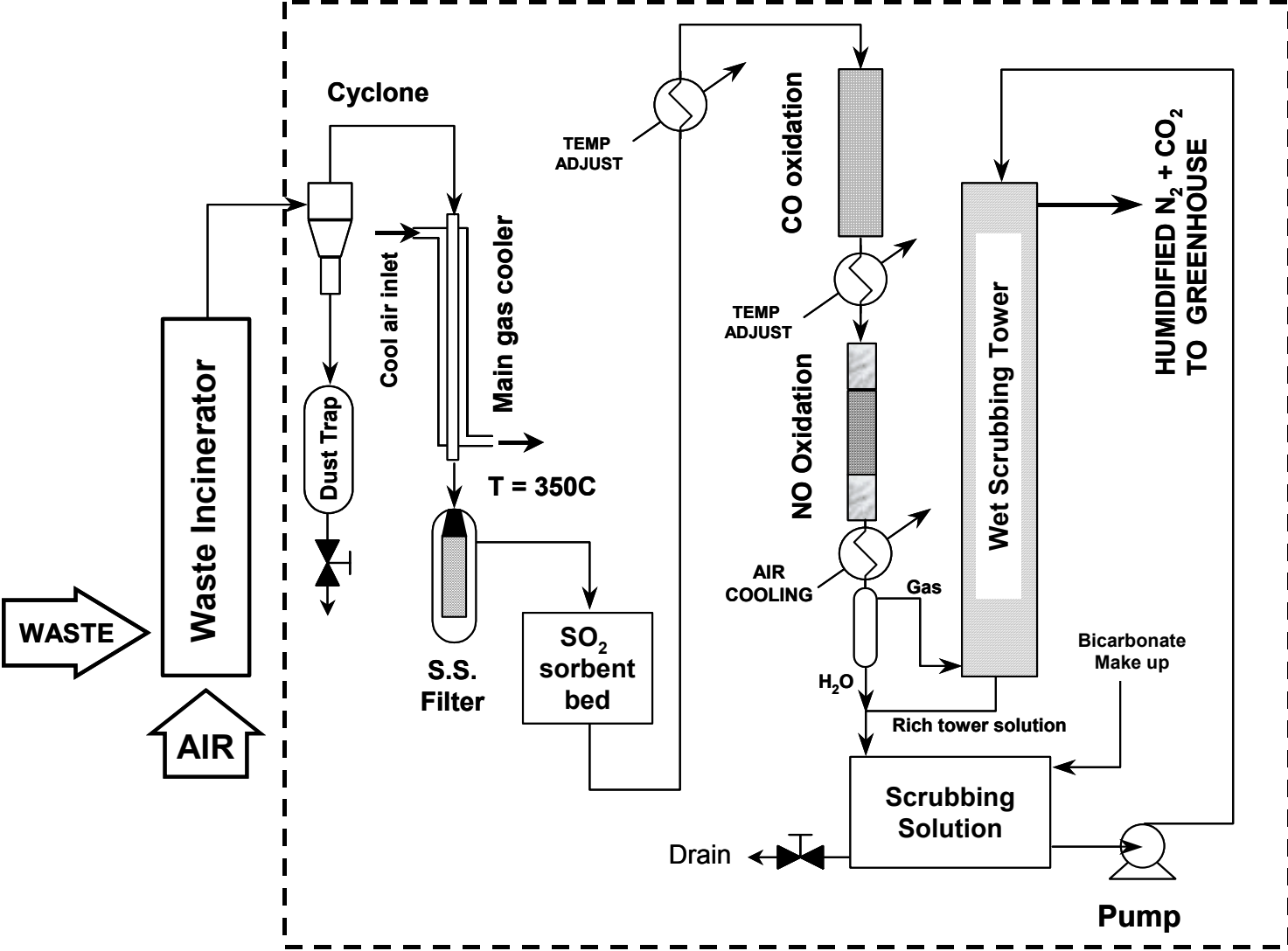
Total design flow = 40 liters/min

*Fisher et al. 1998, SAE 981758; [†] Measured SO₂ < 1 ppm.

System Components

- **Components for process control.**
- **Hardware to remove particulate and cool effluent to 450°C.**
 - Cyclone.
 - Primary heat exchanger.
 - Filter.
- **Fixed bed SO₂ sorbent at 450°C.**
- **HC (CO) oxidation catalyst at 400°C.**
- **NO oxidation catalyst at 260°C.**
- **NO₂ scrubber and H₂O knockout at 25°C.**
- **Carbon bed to remove trace levels of NO.**

TDA Waste Treatment System



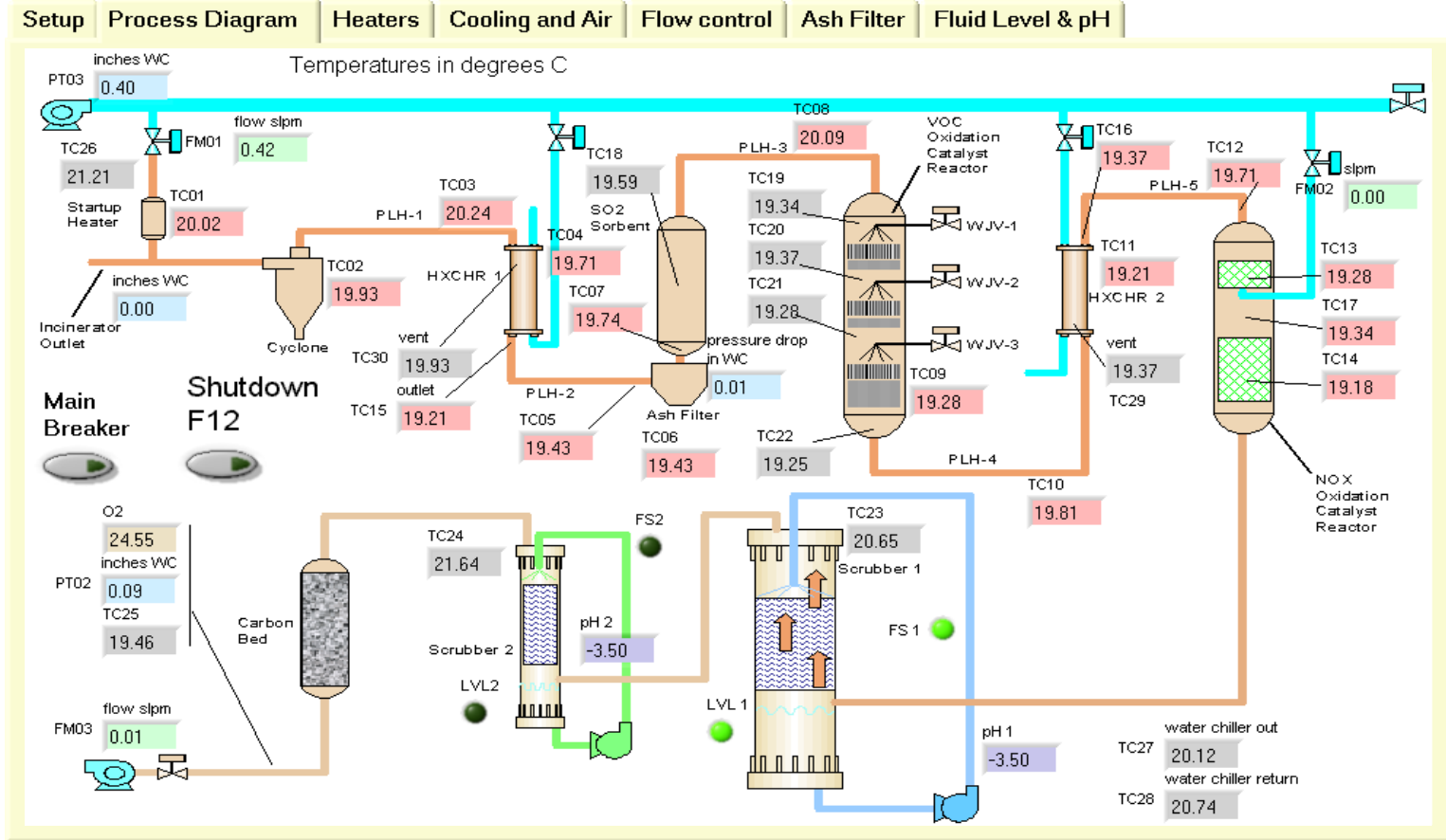
Full Scale Apparatus



Full Scale Apparatus



Labview Software used for System Control



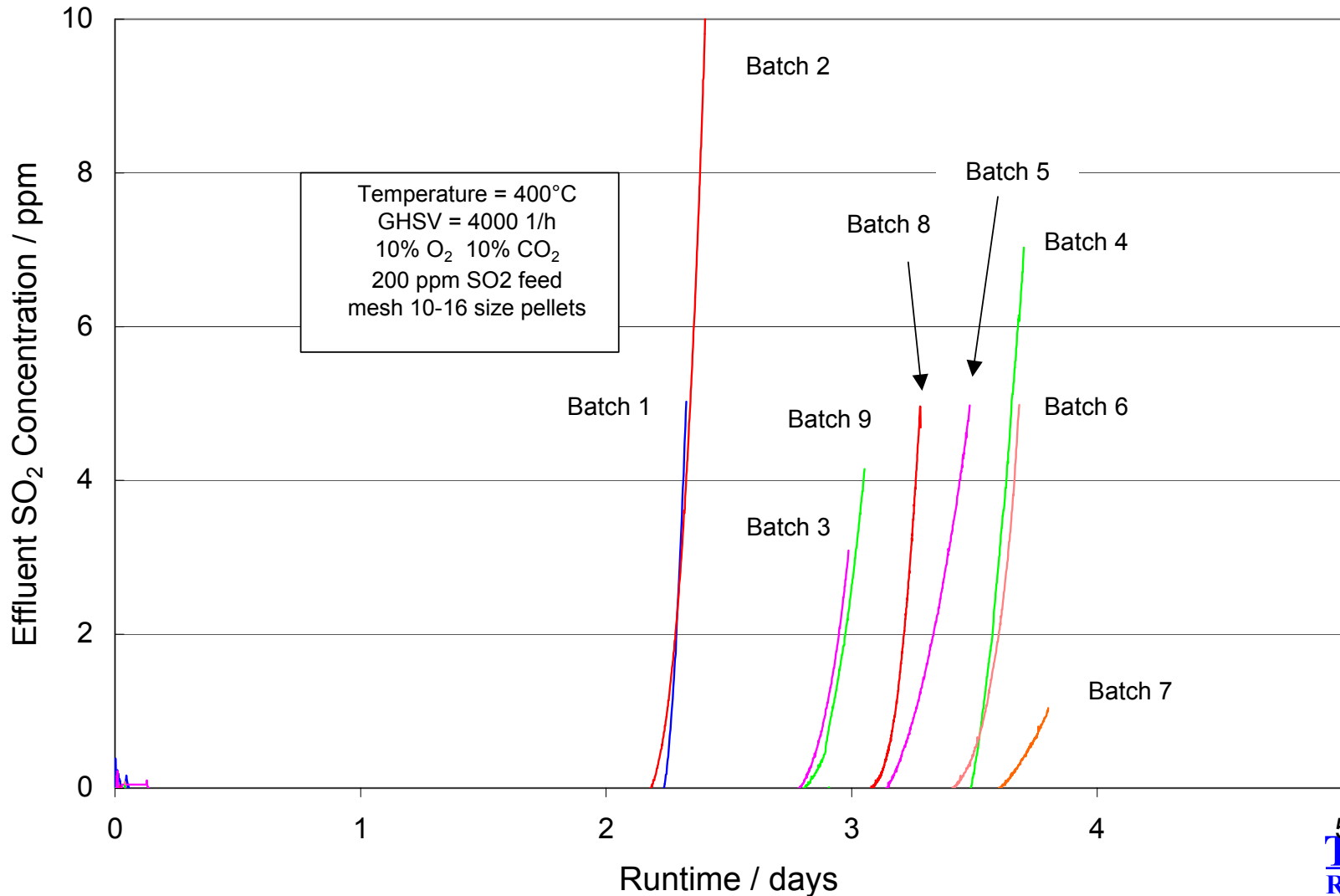
Sulfur Dioxide Removal

- **SO₂ SMAC 2.6 mg/m³ – 0.91 ppm**
- **Commercial methods have been developed to remove SO₂ from flue gas for coal fired power plants - for example:**
 - Wet scrubbing (e.g CaCO₃ slurries)
 - Dry scrubbing (e.g Na₂CO₃ injection)
- **Our choice**
 - Fixed Bed - Na₂CO₃ absorber

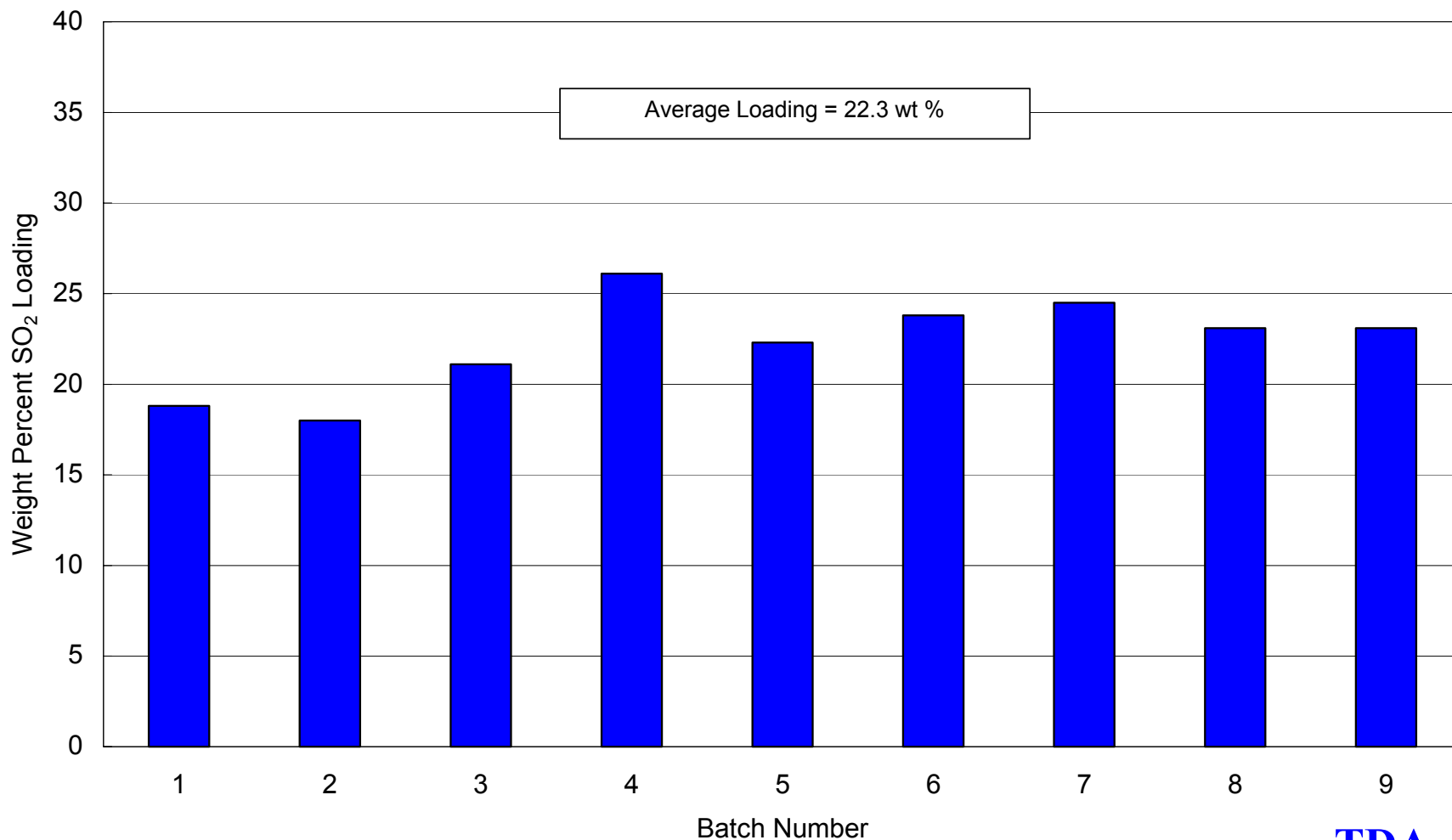


- Prepared nine 330 cc batches of sorbent.

SO₂ Sorbents Were Effective for Several Days



SO₂ Sorbents Exhibited Consistent Loadings



NO_x Control

- **NO SMAC = 6.1 mg/m³ or 4.5 ppm.**
- **NO₂ SMAC = 0.94 mg/m³ or 0.46 ppm.**
- **Current technologies:**
 - Selective Reduction (catalytic and non catalytic).
 - Reducing agent must react with NO instead of O₂.
 - $3 \text{ NO} + 2 \text{ NH}_3 \rightarrow 5/2 \text{ N}_2 + 3 \text{ H}_2\text{O}.$
 - Combustion modification (reducing temperature) - only moderately effective.
 - To date, no catalyst has been identified that is active for the direct decomposition of NO into N₂ and O₂.

NO_x Removal by Oxidation and Scrubbing

- **Take advantage of excess oxygen in effluent stream to catalytically oxidize NO (90% of NO_x) to NO₂.**
- **Use a wet scrubber to remove NO₂ from the waste stream (NO has a low solubility in water and therefore cannot be scrubbed).**

Chemical Reactions

- **Oxidation**

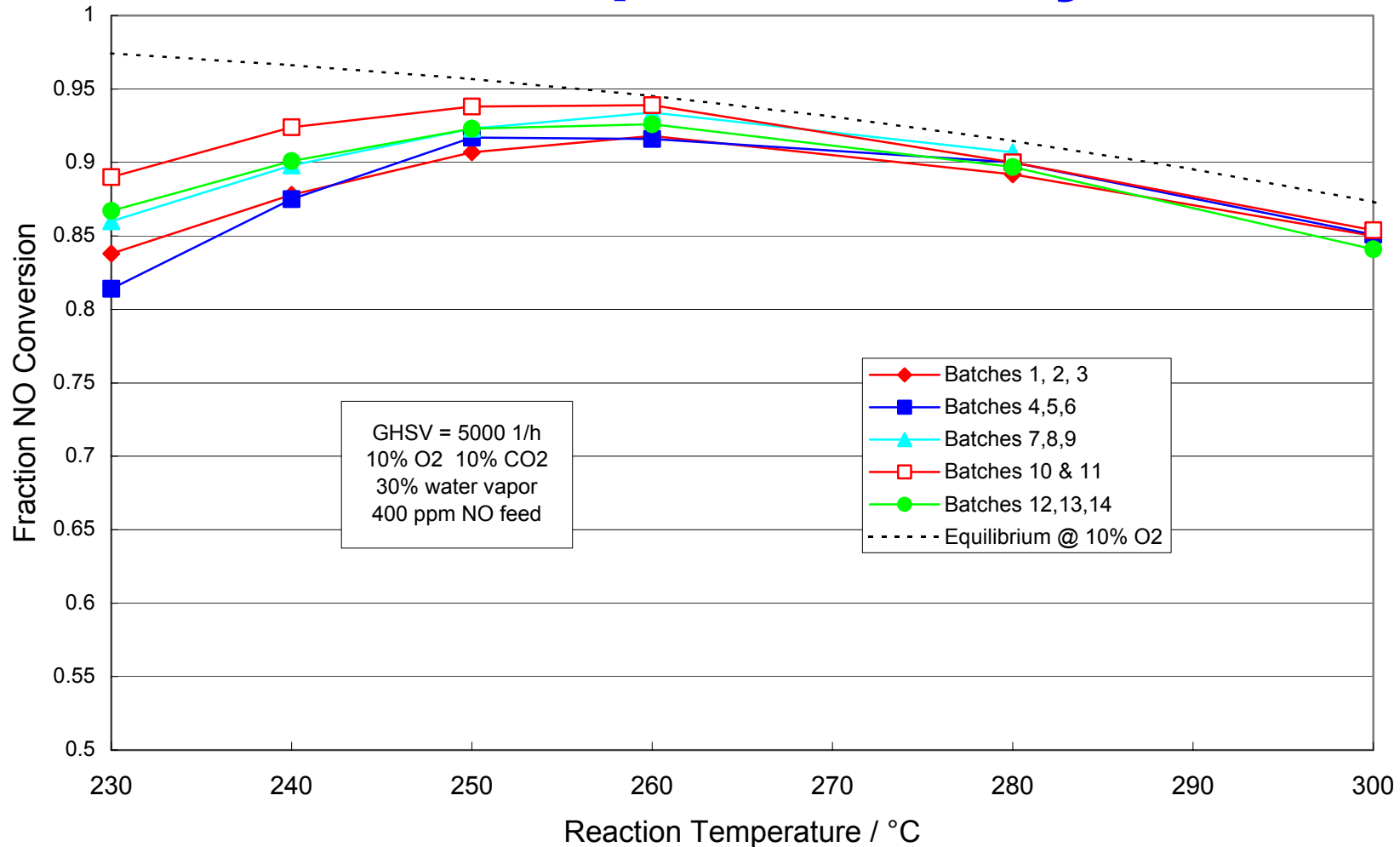
- $\text{NO} + 1/2 \text{O}_2 \rightarrow \text{NO}_2$
- Occurs rapidly on catalyst, slowly in air.
- Must be done at temperatures below 300°C.

- **Adsorption and neutralization of NO_2**

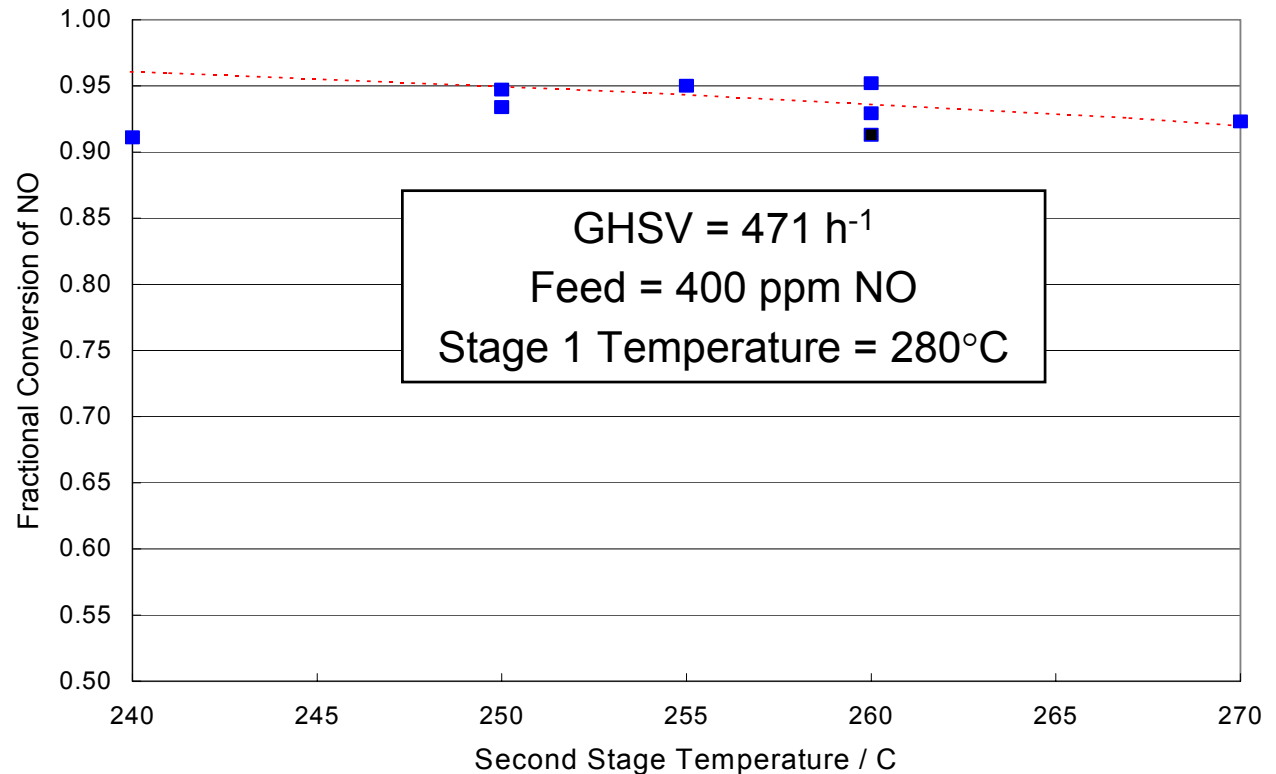
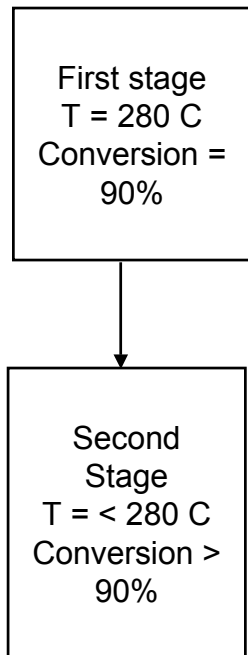
- $2 \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_2$
- Strongly favored by thermodynamics at low concentrations.
- $\text{HNO}_3 + \text{HNO}_2 + 2 \text{NaOH} \rightarrow \text{NaNO}_3 + \text{NaNO}_2 + 2\text{H}_2\text{O}$.

- **Prepared nine batches of NO oxidation catalyst.**

Composite Batches Showed Good Reproducibility



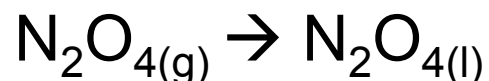
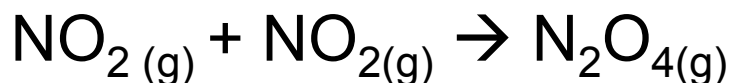
Two Stage Oxidation Unit Produces High NO to NO₂ Conversion



Removal of NO_2 from the Effluent

- Our original approach was to scrub NO_2 in water, forming HNO_2 and HNO_3 .
- Neutralization with NaOH produces NaNO_3 and NaNO_2 .
- Scrubber also serves as water knock-out.
- With 50% water and 400 ppm NO , concentrations of NaNO_2 and NaNO_3 are 1518 and 1870 ppm respectively.
- Could be used as plant nutrients.

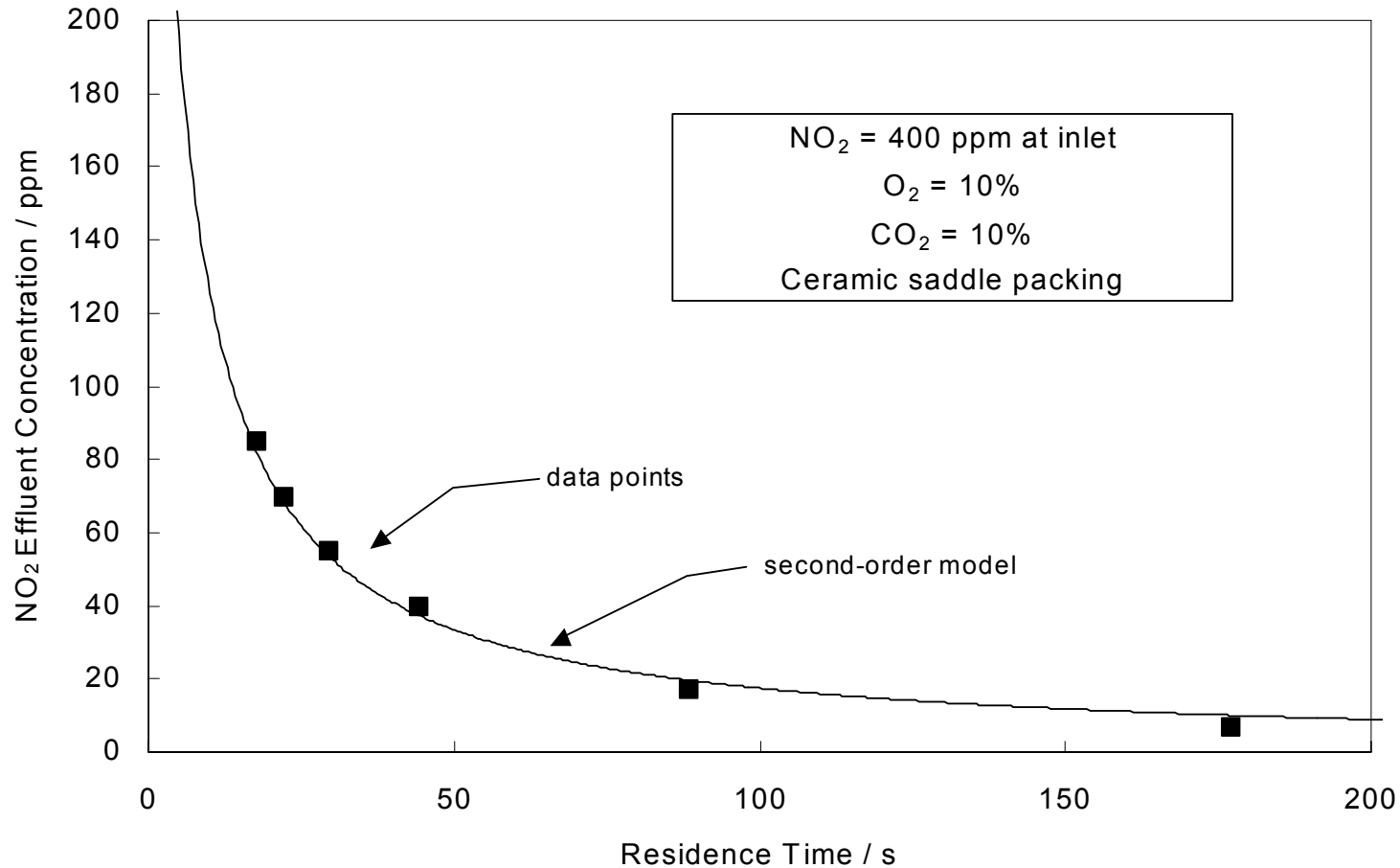
Kinetics of NO₂ Adsorption in Water



$$\text{Rate of Absorption} = k P_{(\text{NO}_2)}^2$$

Rate is fast at high concentrations
but very slow at low concentrations.

NO₂ Removal is Slow at Low Concentrations



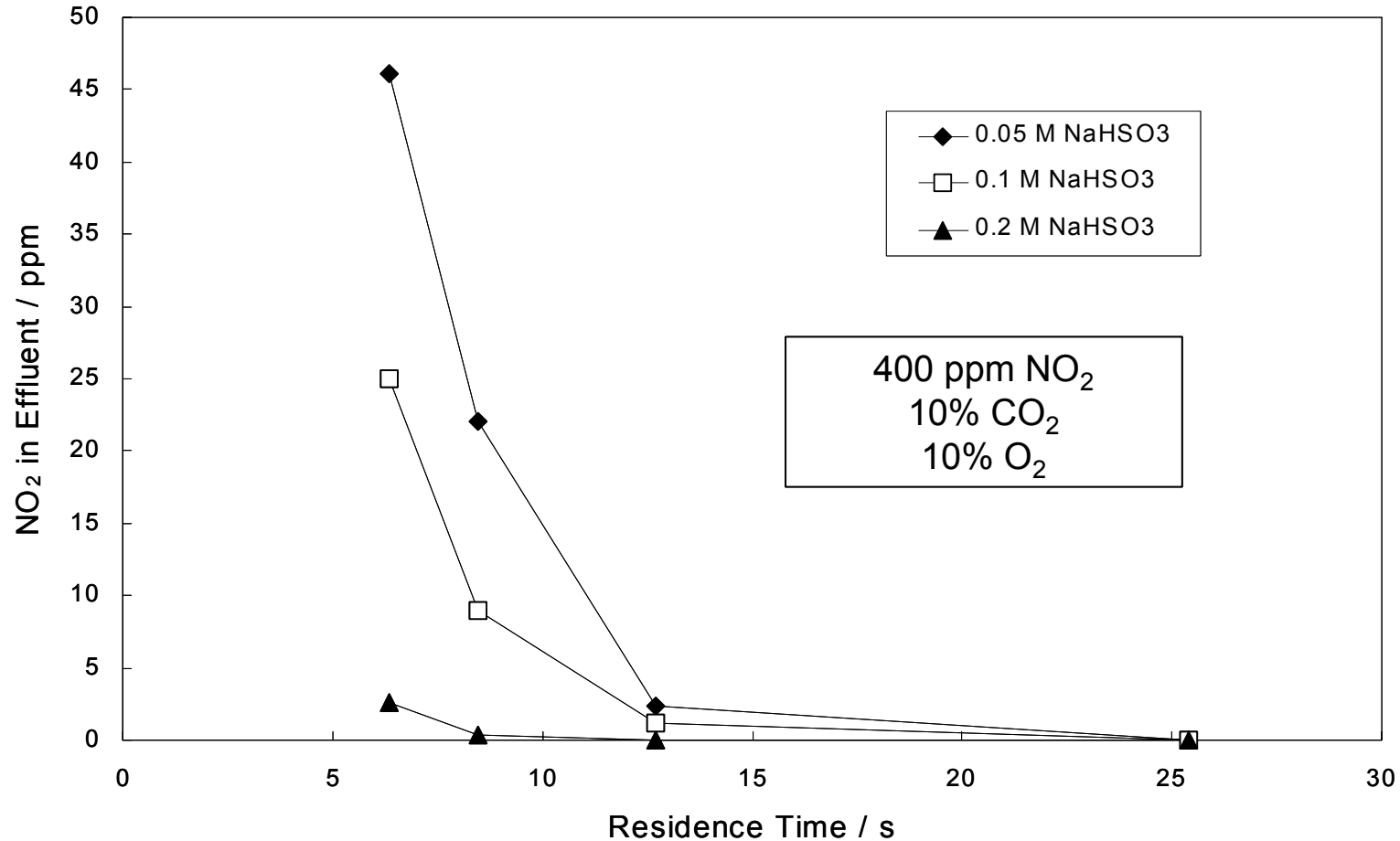
Residence time of 700 seconds required to meet SMAC of 0.46 ppm.

Alternative Scrubbing Approach

- **React NO₂ with an aqueous reducing agent in the presence of a catalyst*.**
 - $R(NH_2) + NO_2 \rightarrow 1/2 N_2 + R(NH_2-O_2)$
 - $R(NH_2-O_2) + 2 NaHSO_3 \rightarrow R(NH_2) + 2NaHSO_4.$
- **Reaction is very rapid and does not have second order dependency on NO₂.**

* Senjo and Kobayashi, 1977

Reducing Solution Rapidly Removes NO₂



400 ppm NO₂
10% CO₂
10% O₂

This solution is very effective for NO₂
even at very short residence times.

Tradeoffs for Each Scrubber

- **Single scrubber with water.**
 - + Reagent weight of 31 lbs per year (NaOH).
 - + Neutralized liquid can be used for plants.
 - - Column size: 15-in OD x 21-ft;
 - - Weight = over 400 lbs.
- **Single scrubber with bisulfite.**
 - + Column size is 6-in x 3.3 ft.
 - + Weight less than 10 lbs.
 - - Reagent weight of 150 lbs per year.
 - - Liquid effluent must be treated by RO.

Use of Two Scrubbers in Series

- Assume water scrubber is first, followed by bisulfite solution.
- Assume various concentrations of NO_2 in the effluent of the water scrubber.
- Assume balance of NO_2 is removed in the reducing scrubber.
- Calculate size and weight of the water scrubber along with reagent weights for both units.

Water and Bisulfite Scrubbers

Water scrubber

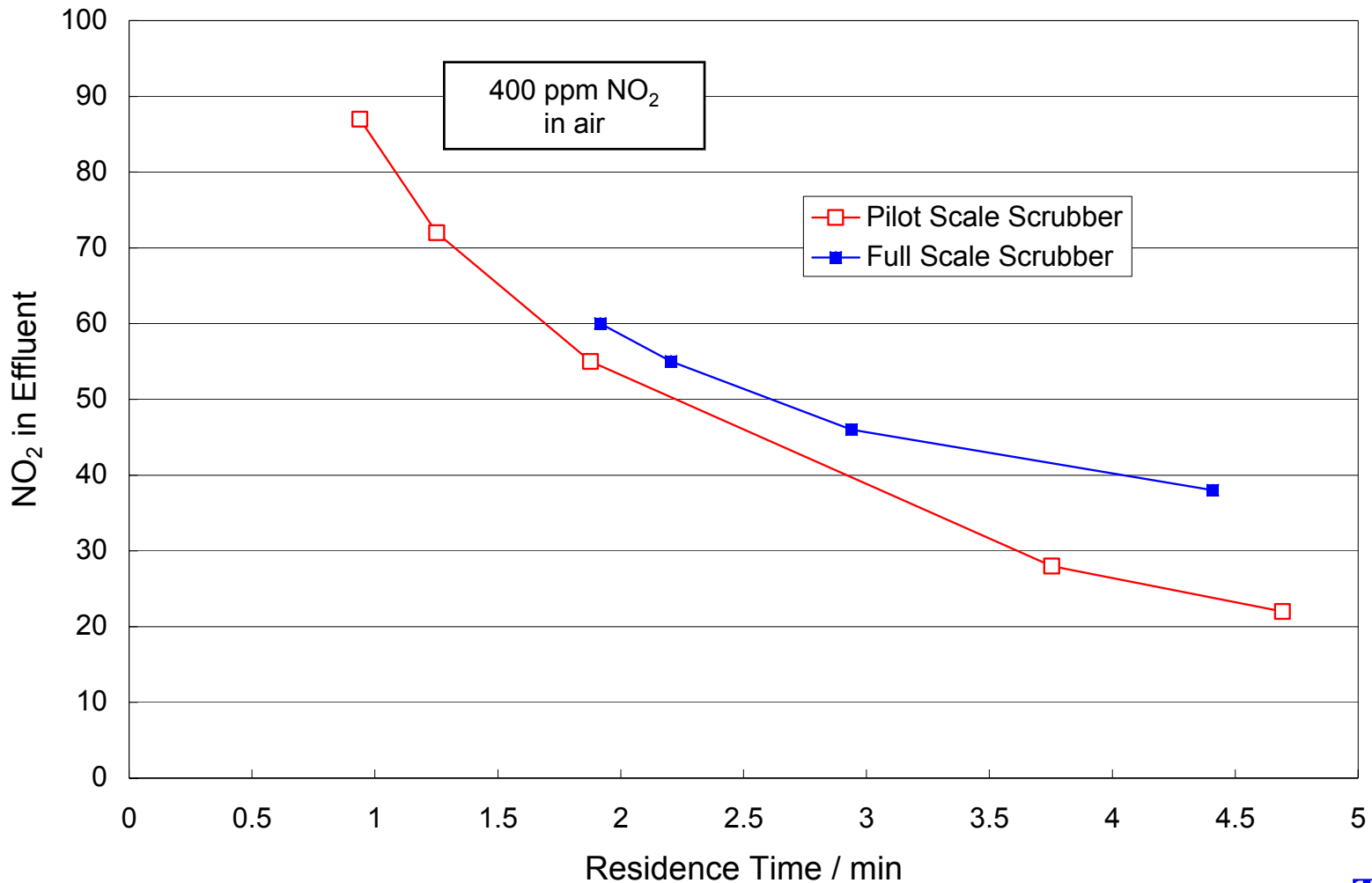
Reduces NO_2
concentration from
400 to 50 ppm.



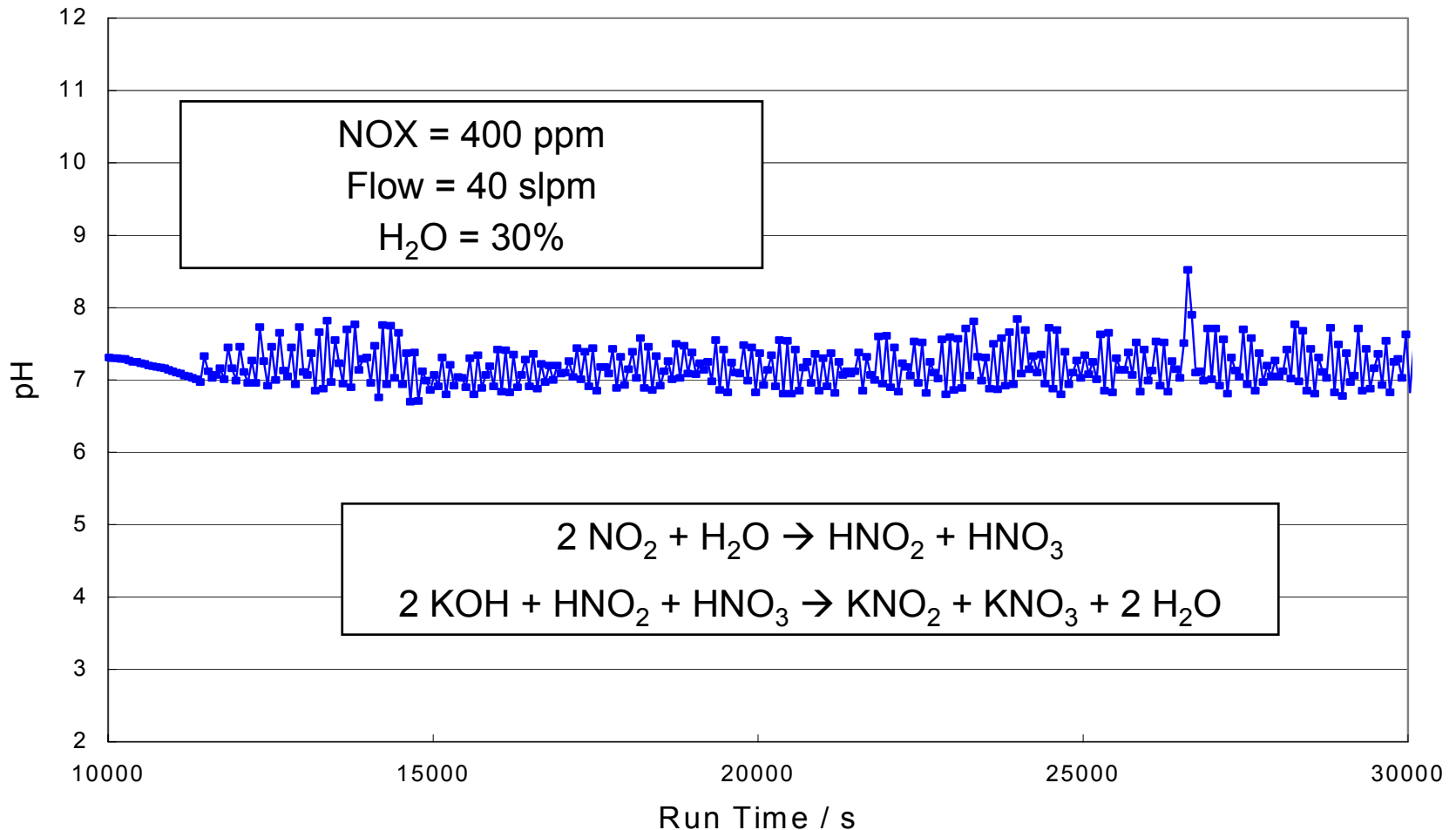
Bisulfite scrubber

Reduces NO_2
concentration 50 to
< 0.1 ppm.

Water Scrubber is Effective for NO₂ Removal at High Concentrations



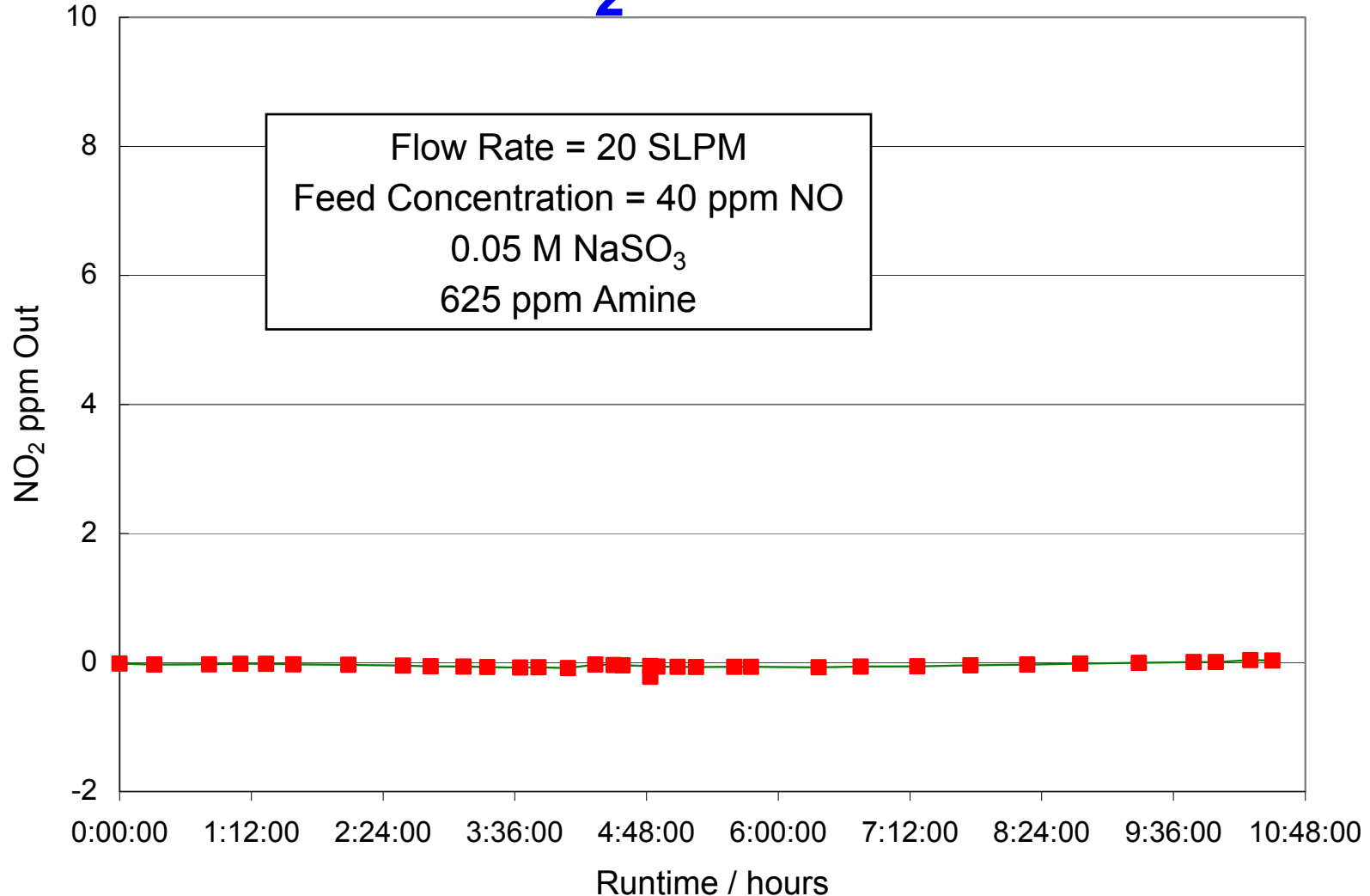
Automated KOH Addition Controls pH in Water Scrubber



We Achieved a Good Material Balance with the Water Scrubber

| | | |
|---------------|----------------------------|---------------------------------|
| Flow In | Concentration | 400 ppm |
| | Flow Rate | 40 slpm |
| | NO _x Flow | 7.14E-4 moles/min |
| Flow Out | Concentration | 115 ppm (NO + NO ₂) |
| | Flow Rate | 28 slpm |
| | NO _x Flow | 1.44 E-4 moles/min |
| Accumulation | Rate | 5.60E-4 moles/min |
| | NO _x in 6.6 hrs | 0.222 moles |
| Base Addition | KOH | 0.237 moles |
| | Difference | 6.7% |

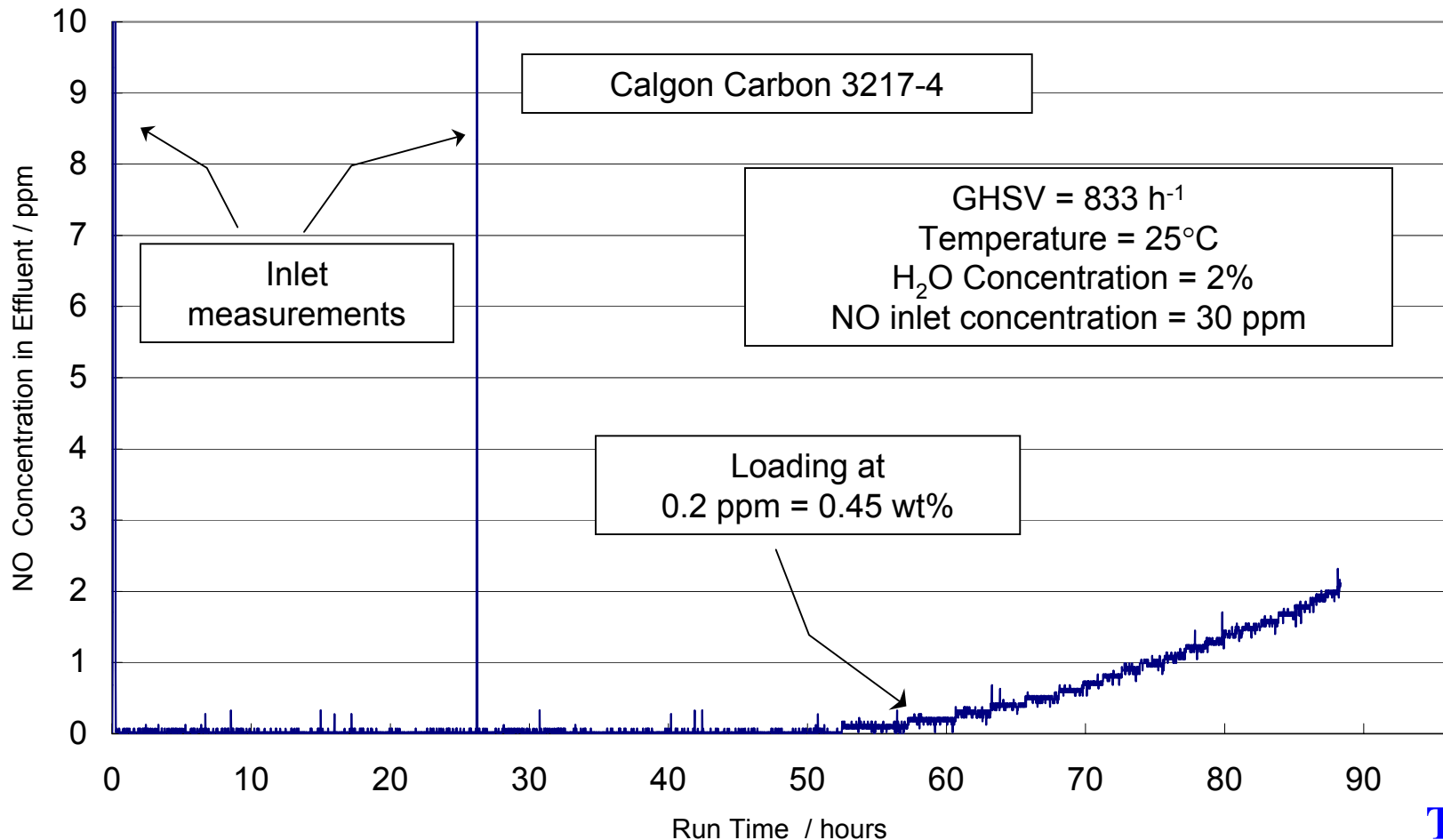
Bisulfate Scrubber is Very Effective at Low NO₂ Concentrations



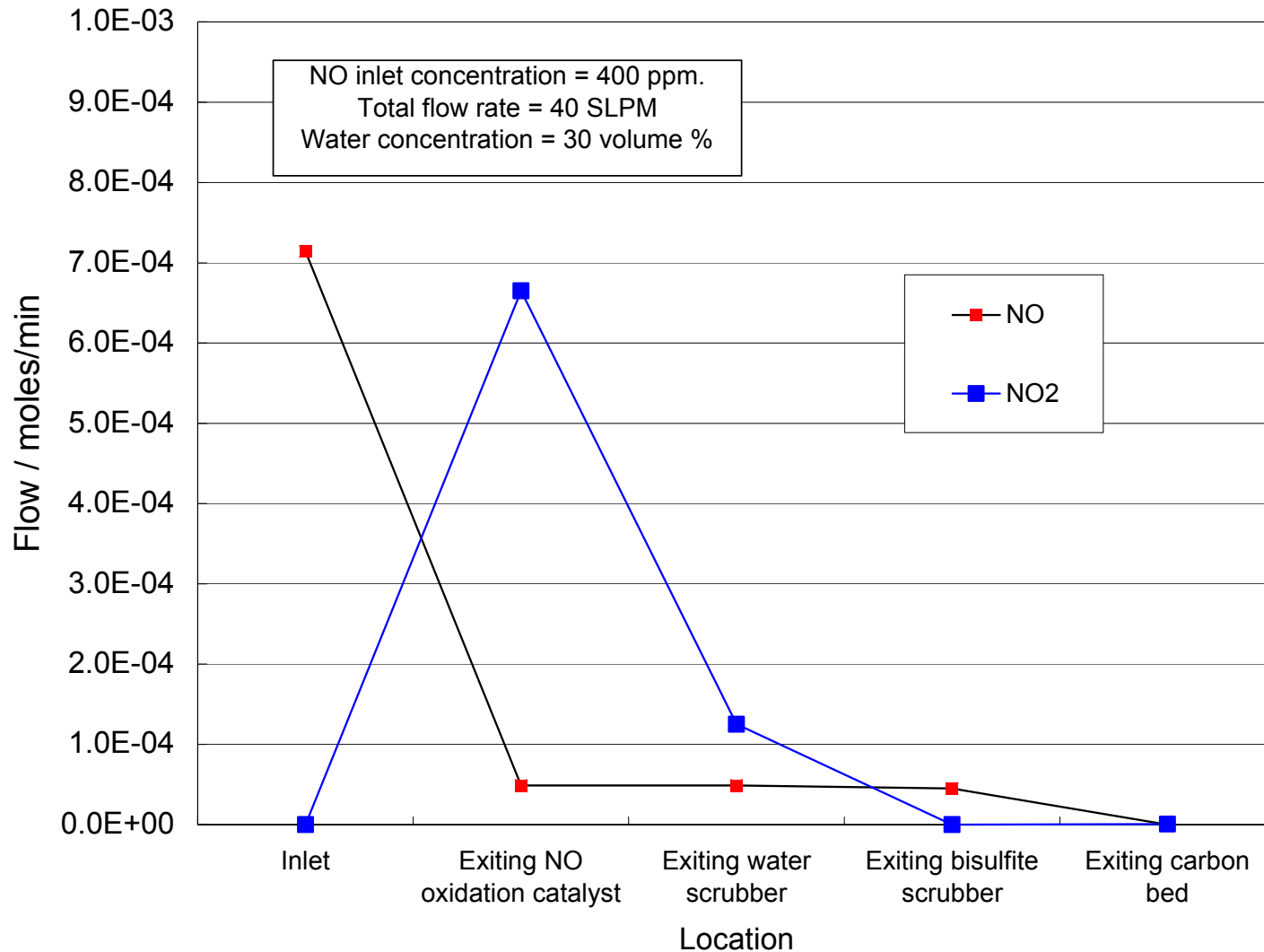
Carbon Bed

- Needed to absorb low levels of NO.
- At 97.5% conversion of NO to NO₂, about 0.6 lbs of NO would be generated in one year.
- TDA obtained active material from Calgon.
- NASA Ames Research Center has developed carbon for NO control.

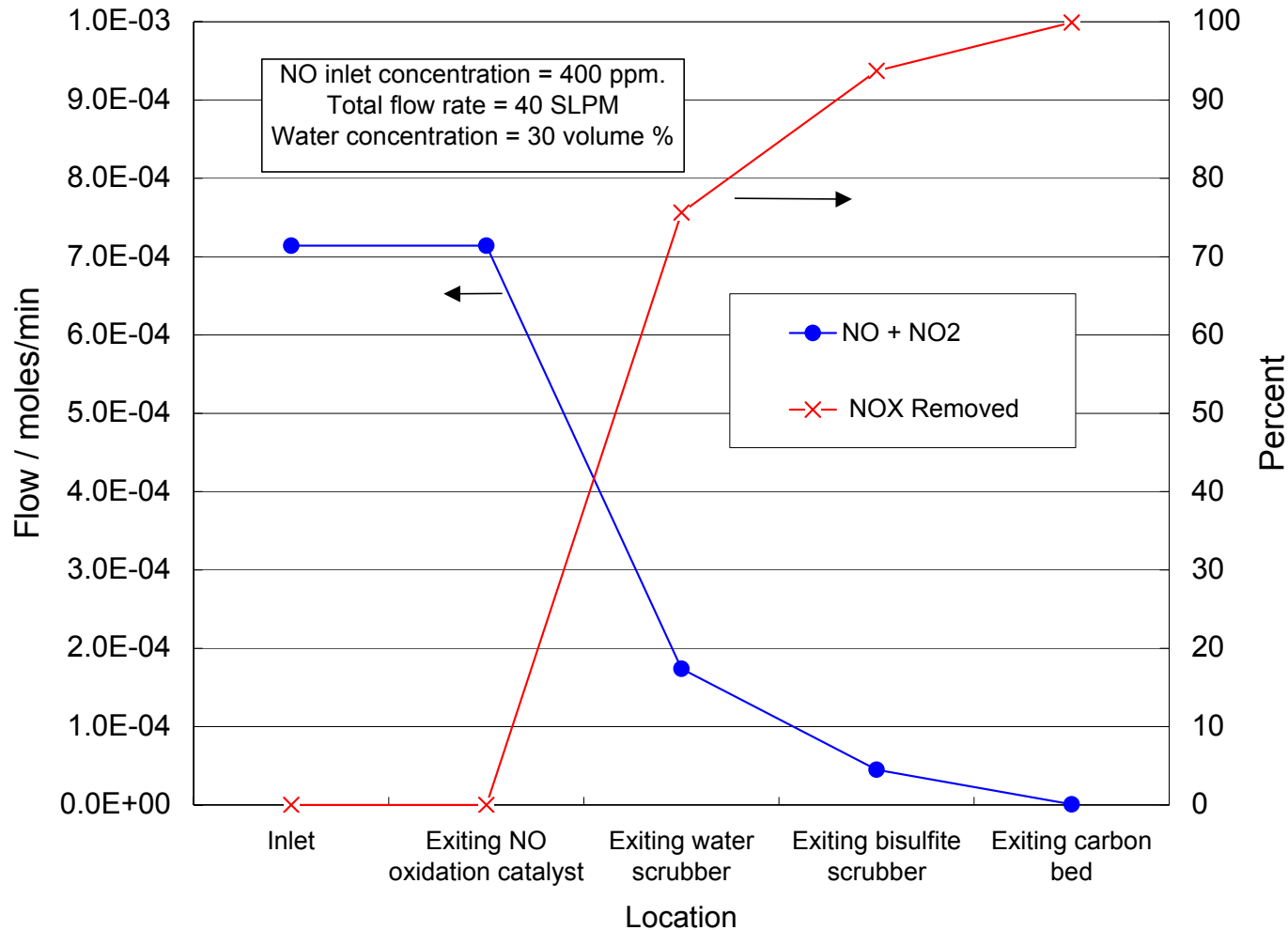
Carbon Bed to Remove Trace Levels of NO



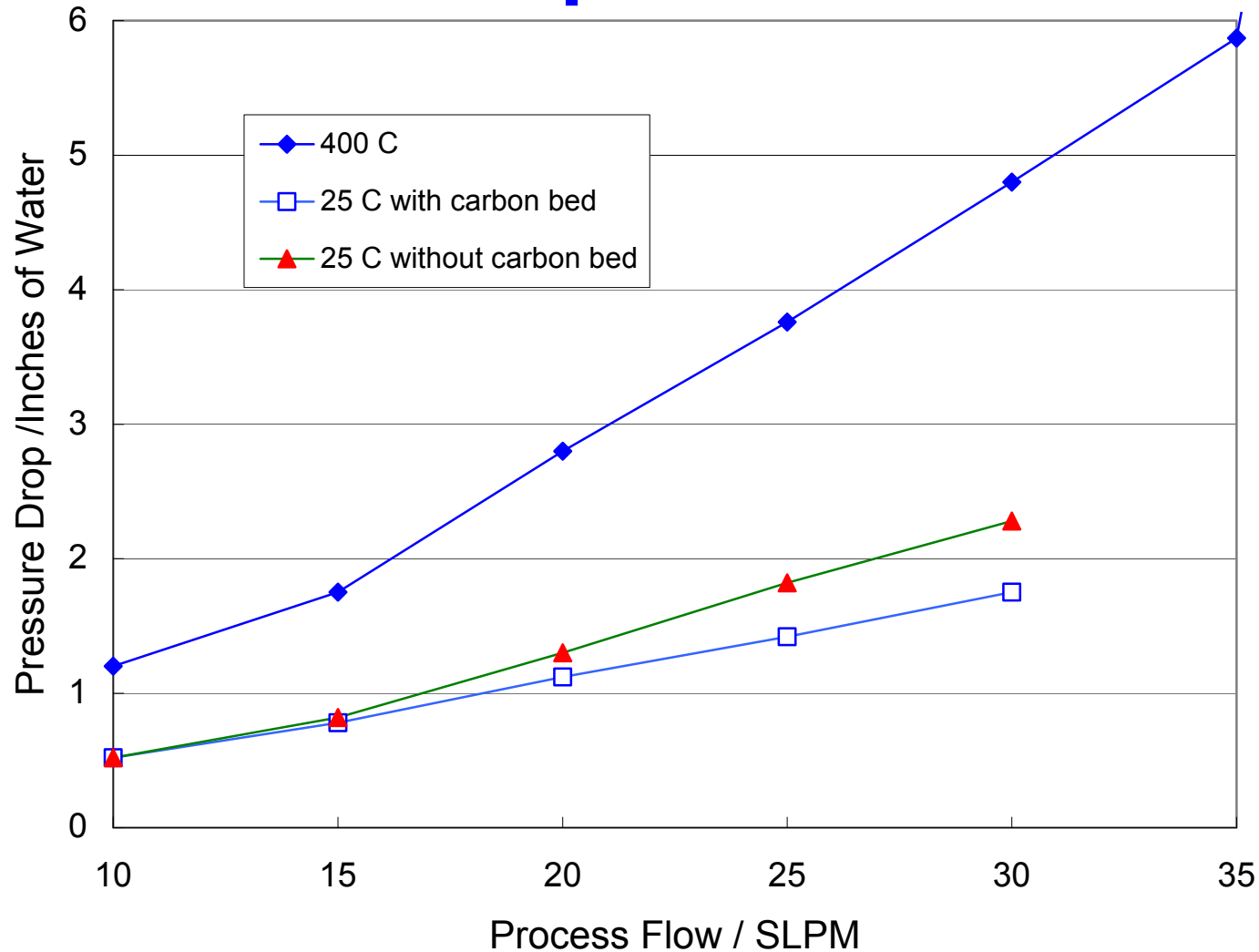
NO Converted to NO₂ then Removed from the Flow



System Achieves over 99% NO_x Elimination



The System Met Pressure Drop Requirements



Summary and Conclusions

- TDA has designed and constructed a system to treat incinerator effluents.
- NO_x will be removed by oxidation and scrubbing using TDA oxidation catalyst.
- NO_2 scrubbing is accomplished by two scrubbers in series.
- The integrated system is complete and performs as designed.

Acknowledgements

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